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USSR: Chemistry

FBIS 50th Anniversary Note

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This year the Foreign Broadcast Information Service observes its 50th anniversary.

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We members of the current staff of FBIS extend our thanks to consumers for their interest in FBIS products. To past staffers we extend our thanks for helping the service reach this anniversary year. At the same time, we pledge our continued commitment to providing a useful information service.



R. W. Manners
Director

Foreign Broadcast Information Service

Science & Technology

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UDC 543.432.062

Concurrent Determination of Niobium and Tantalum by Using Bromopyrogallic Red in the Presence of Cetylpyridinium Bromide and Triton X-305

917M0020A Kiev UKRAINSKIY KHIMICHESKIY
ZHURNAL in Russian Vol 56 No 9, Sep 90
(manuscript received 1 Nov 89) pp 944-948

[Article by A.T. Pilipenko, A.N. Masko, and Ye.G. Maksimyuk, Kiev University]

[Abstract] Optimal conditions for the formation of tantalum (V) and niobium (V) complexes with bromopyrogallic red (BPR) modified with the surface-active reagent cetylpyridinium bromide (CPB) were studied, and their spectrophotometric characteristics were determined to develop a method for concurrent determination of niobium and tantalum. It was determined that in order to obtain maximum development of the color, the metal solutions had to be added last, i.e., after the BPR-CPB associates have already been formed. Calculation of the niobium and tantalum concentrations were carried out on the basis of readings obtained at 20 analytical wavelengths by using the Firardt method and the computer program Spektr. Relative measurement error, determined from the analysis of known mixtures, was found to be 1.7-8.3% for tantalum and 1.3-15.0% for niobium. This method is applicable to binary mixtures in which the component relationship can vary from 1:7 to 7:1. Figures 3; references 7: 5 Russian, 2 Western.

UDC 543.422:546.73

Atomic Absorption Determination of Cobalt in Hypochlorite Solutions

917M0020B Kiev UKRAINSKIY KHIMICHESKIY
ZHURNAL in Russian Vol 56 No 9, Sep 90
(manuscript received 4 Aug 89) pp 951-954

[Article by G.S. Lisetskaya, N.S. Bilerko, and V.V. Zayets, Kiev Branch of State Scientific Research Institute of Chlorine Project]

[Abstract] The goal of this study was to develop an atomic absorption method for determination of cobalt in hypochlorite solutions in the concentration range from 0.05 to 2.0 mg/dm³. These solutions also contain up to 150 g/dm³ sodium chloride and 10 g/dm³ sodium chlorate. Direct-flame atomic absorption of cobalt was not possible because of the low sensitivity of this method and the high salt content of the medium. Therefore an electrothermal "graphite oven" atomizer was used in the method being reported. The cobalt determination was performed at two wavelengths, i.e., $\lambda = 240.7$ nm for the concentration range of 0.04-0.5 mg/dm³ and $\lambda = 252.1$ nm for 0.20-2.0 mg/dm³. The relative measurement error of this method was 15% with a P value of 0.95. Figures 2; references: 4 (Russian).

UDC 536.7

Heat Capacity of Praseodymium in the Interval Between 5.6 and 314 K

917M0026G Moscow ZHURNAL FIZICHESKOY
KHIMII in Russian Vol 64 No 10, Oct 90 (manuscript
received 10 Nov 89) pp 2636-2640

[Article by G.A. Berezovskiy, G.S. Burkhanov, N.B. Kolchugina, I.Ye. Paukov, A.B. Tagayev, and O.D. Chistyakov, Institute of Inorganic Chemistry, Siberian Department, USSR Academy of Sciences, Novosibirsk, and Metallurgy Institute imeni A.A. Baykov, Moscow]

[Abstract] The literature includes a series of studies examining the heat capacity of praseodymium (C_p) in different temperature intervals. The authors of the study reported herein measured the heat capacity of a high-purity praseodymium with a resistance ratio of 78.5 in the temperature interval from 5 to 320 K. They used the vacuum adiabatic calorimetry method to measure the heat capacity of praseodymium at 154 experimental points. Next, they plotted the function $C_p(T)$. At temperatures below 10 K the mean deviation of the experimental heat capacity values from the smoothed curve representing $C_p(T)$ amounted to about 1.0%; at higher temperatures it was less than 0.1%. The authors' results were found to be in good agreement with those appearing in several other publications. Their findings do, however, cast doubt on a previously published assertion regarding antiferromagnetism in praseodymium below 25 K. Figures 2, tables 2; references 11: 3 Russian, 8 Western.

UDC 541.128:542.941.73:547.821

Liquid-Phase Hydrogenation of Pyridine in a Nickel-Chromium Catalyst

917M0019A Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSTANSSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 4, Jul-Aug 90 (manuscript received 16 Jan 90) pp 20-23

[Article by A. Ualikhanova, A.A. Dembitskiy, and D.V. Sokolskiy, Institute of Organic Catalysis and Electrochemistry imeni D.V. Sokolskiy]

[Abstract] Initial research on the hydrogenation of pyridine in the presence of gaseous-phase nickel yielded trace quantities of piperidine. The yields were later increased by combining the use of nickel catalysts with elevated pressures and temperatures and later by applying nickel catalysts onto different oxides. In a continuation of this line of research, the authors of this study examined the catalytic properties of a nickel-chromium catalyst during the hydrogenation of pyridine and the kinetic laws governing this process. First, pyridine was distilled in a vacuum. The quantity of pyridine in the hydrogen equivalent was varied from 400 to 1,600 cm³. The reaction was conducted in the presence of tablets of a commercially produced nickel-chromium catalyst. Its total surface amounted to 42.4 m²/g. A constant pressure was maintained throughout each reaction. During the experiments, the temperature was varied from 373 to 453 K, and the hydrogen pressure was varied from 2 to 8 MPa. The catalyst was analyzed by gas-liquid chromatography at temperatures of 353 and 4653 K in a 2,800 x 5-mm column with 10% PEG-1540 + 1% KOH. It was discovered that, with respect to hydrogen, the reaction was close to a first-order reaction (0.7), whereas with respect to pyridine, it was close to a zero-order reaction (0.1). The apparent activation energy amounted to 89-90 kJ/mol. At a pressure of 8 MPa and a temperature of 423 K, the piperidine yield was greater on a nickel-chromium contact (99.5%) than on an NiR contact (98.6%). The content of by-products in the catalyst did not exceed 0.7%. Figures 2, table 1; references 22: 15 Russian, 7 Western.

UDC 669.72.15:622.7

Kinetics of the Synthesis of Polymethylphenylsilane Under the Effect of Acoustic Cavitation

917M0026F Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 64 No 10, Oct 90 (manuscript received 27 Oct 89) pp 2641-2646

[Article by G.P. Los, A.A. Savitskiy, I.I. Skorokhodov, and O.I. Zinovyev, State Scientific Research Institute of the Chemistry and Technology of Elemental Organic Compounds, Moscow]

[Abstract] By way of the example of the reaction of the condensation of methylphenyldichlorosilane and metallic sodium in toluene at 100°C, the authors of the study reported herein examined the kinetics of the transformation of dihalogensilanes into oligomer polysilanes under and apart from the effect of acoustic cavitation. To a triple-necked glass column (capacity, 100 m³) containing 50 ml toluene and 4.8 g Na, they added 16.2 ml methylphenyldichlorosilane. The contents of the column were then subjected to ultrasound waves with a frequency of 22 kHz, with a total of 50 W being directed into the liquid. The subsequent analyses were conducted by the techniques of gas-liquid and gel permeation chromatography. It was discovered that both with and without the application of ultrasound a mixture of oligomer polysilanes having both cyclic and linear molecular structures was formed. It was further demonstrated that the application of ultrasound results in mutual oscillatory transformations of these structures and ultimately in the complete transition of those polysilanes having a linear structure into polysilanes with a cyclic structure. A heterogeneous analogue of the Belousov-Zhabotinskiy reaction was discovered. The results of the experiments conducted led the authors to conclude that in the system studied, active particles appear under the effect of acoustic cavitation. They participate in the development of oscillatory processes by accelerating the reactions of the transformation of chain oligomers into a cyclic derivative and by entering into an autocatalytic reaction resulting in the formation of active oligomer chain molecules. Figures 4, tables 1; references 5: 1 Russian, 4 Western.

UDC 541.128:546.215

Stability of Oxygen Electrode Catalyst Based on Cobalt Tetra- para-nitrophenylporphine and a Carbon Carrier

917M0030A Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNOLOGIYA in Russian Vol 33, No 9, Sep 90 (manuscript received 25 Dec 89) pp 27-30

[Article by S. N. Pobedinskiy, A. A. Trofimenko and N. P. Novikova, Department of Physical Chemistry, Ivanovo Chemical- Technological Institute]

[Abstract] The goal of this work was to investigate the stability of an oxygen electrode in an alkaline electrolyte containing a cobalt complex of tetra-(p-nitro)-phenylporphine deposited on acetylene carbon black as the catalyst. The effect of electrolyte temperature, the current density and the contact time with the alkaline solution on the stability of this electrode was investigated showing that the electrode potential dropped with time, the rate of this decrease increasing with increasing temperature and current density. Electrochemical activity of the electrode diminished with increased time of cathode polarization, evidently due to the deactivation of the catalyst which is directly related to the breakdown of the cobalt complex occurring during

its reaction with hydrogen peroxide which forms as an intermediate product of the electro-reduction of oxygen. Figures 4; references: 3 (Russian).

UDC 542.97.976.3

Investigation of Sublimation Process of Non-platinum Catalyst Components at High Temperature

917M0030B Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA in Russian Vol 33, No 9, Sep 90 (manuscript received 24 Mar 89) pp 49-52

[Article by V.F. Chernyy, N.F. Kleshchev, Nidal Makhmud El-Hatib and N.G. Petrenko, Department of Analytical Chemistry, Kharkov Polytechnical Institute imeni V.I. Lenin]

[Abstract] The goal of this work was to explain the effect of temperature on the extent of sublimation of metal oxides, their effect on the oxidation of ammonia to nitrogen II oxide and to determine the temperature of the beginning of sublimation. The study catalyst had the following composition: Fe_2O_3 - 90%; Cr_2O_3 - 7% and Al_2O_3 - 3%. It was determined that under the reaction conditions used, minute quantities of the components of catalyst exist in the gaseous phase and their presence affects the selectivity of the catalyst, and the yield of nitrogen II oxide. The temperature interval corresponding to the highest activity of the catalyst coincided with the temperature of maximum carry-off of iron. Maximum reaction effect was observed with about a 6.0 mg/h total carry-off of iron and chromium ions. Figures 2; references: 2 (Russian).

UDC 661.566

Determination of Kinetic Parameters of Ammonium Oxidation Over Iron Oxide Catalyst

917M0030C Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA in Russian Vol 33, No 9, Sep 90 (manuscript received 27 Mar 89) pp 53-55

[Article by A.A. Lukovenko, Nguen Hyu Tho, A.S. Savenkov, A.Ya. Loboyko and V.V. Ivanov, Department

of Inorganic Compounds Technology, Kharkov Polytechnical Institute imeni V. I. Lenin]

[Abstract] In an attempt to find the most active and selective catalyst, the temperatures of "extinction" and "ignition" of five different iron (III) oxide catalysts were determined at different flow rates of the ammonia-air mixture. Temperature limits of the existence of kinetic and external diffusion regimens were determined. The selectivity of the catalyst seemed to be inversely related to all parameters studied. The optimal working temperature for the best catalyst was 1123-1223 K. On the basis of experimental data, an iron (III) oxide catalyst was developed assuring high degree of ammonia conversion to nitrogen (II) oxide (95-96%). Figures 2; references 5: 4 Russian, 1 Western (1 by Russian author).

UDC 66.097.3+52.626

Effect of Laser Radiation on Activity of Impregnated Catalysts

917M0030D Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA in Russian Vol 33, No 9, Sep 90 (manuscript received 8 Jan 90) pp 122-123

[Article by V.Ye. Myasoyedov, O.A. Samsonov and M.I. Voronova, Department of Inorganic Compounds Technology, Ivanovo Chemical-Technology Institute]

[Abstract] An attempt was made to show the potential of using a low power electromagnetic coherent wave to intensify the production of highly active catalyst for the purification of exhaust gasses from nitrogen oxides. The study subject consisted of aluminum-iron catalyst which was irradiated with a laser beam of 633 nm wavelength during the impregnation process. It was shown that at 800°C the degree of nitrogen oxide reduction increased by about 15% when this catalyst was used. EM data showed that the active component was uniformly distributed over the carrier surface. References: 4 (Russian, 2 by Western authors).

UDC 540.27:546.11:541.133.1

The Kinetics and Mechanism of Water-Hydrogen Isotope Exchange During the Electrotransfer of Hydrogen in a Cell With a Solid Polymer Electrolyte

917M0026E Moscow *ZHURNAL FIZICHESKOY KHIMII* in Russian Vol 64 No 10, Oct 90 (manuscript received 14 Nov 89) pp 2761-2766

[Article by A.B. Morozov and M.B. Rozenkevich, Moscow Chemical Technology Institute imeni D.I. Mendeleev]

[Abstract] The process of the electrotransfer of hydrogen in a cell with a solid polymer electrolyte based on MF-4SK membrane is accompanied by a significant thermodynamic effect due to isotope exchange between the liquid water poured into the cell's cathode space and the hydrogen fed into the anode space. In view of the great promise of using such cells as mass exchangers for use in implementing the process of isotope exchange in a water-hydrogen system, the authors of the study reported herein examined the kinetics and mechanism of the process of water-hydrogen isotope exchange during the electrotransfer of hydrogen in a cell with a solid polymer electrolyte. The cell used in the experiments had an MF-4SK polymer membrane 250 μm thick and platinum anode and cathode electrocatalysts. The membrane had

a working surface of 6.2 cm^2 , the electrocatalyst was applied with a density of 2 mg/cm^2 , and the particle size ranged from 10 to 20 μm . Water was poured into the cathode space, and gaseous hydrogen was fed into the anode space. Potential differences ranging from 0 to 1.23 V were applied to the cell. The isotope make-ups of the hydrogen streams leaving the anode and cathode spaces (or else their combined isotope make-up when they were joined) were analyzed. The molar ratio of the liquid water and hydrogen phases was varied so that the change in the deuterium concentration during the course of the individual experiments could be ignored. The atomic emission spectroscopy analysis was conducted on a DSI-8-3; the relative error of analyzing the isotope make-up of the water was 5%, and that of analyzing the isotope make-up of the hydrogen was 3%. The experiments conducted demonstrated that a cell like the one devised is an effective mass exchange device for implementing ion exchange in a water-hydrogen system. By using a conventional hydrophilic catalyst (Pt applied to a polymer membrane), the authors were able to achieve isotope exchange conditions that were similar to those achieved when hydrophobic catalysts are used. It was established that the anodic process makes the principal contribution to the observed effect. From the standpoint of isotope exchange rate, a current of 0.07 A/cm^2 (temperature, 303 K) proved to be optimal for a 250- μm -thick membrane. Figures 3, table 1; references 6; 4 Russian, 2 Western.

UDC 550.834

Grouping Seismic and Gravimetric Data of Oil and Gas Prospecting

907M0141C Kiev NEFTYANAYA I GASOVAYA PROMYSHLENNOST' in Russian No 1, Jan-Mar 90 (manuscript received 24 Oct 88) pp 16-19

[Article by V.Ye. Burakovskiy, Yu.K. Tyapkin, and S.M. Poznanskiy, Ukrainian Geological Prospecting SRI]

[Abstract] Dependable tracings of outcroppings in lithological-stratigraphic variances have become urgent. Effects of foundation breaks on the formation of structures in sedimentary mantles and hydrocarbon catch-basins are cited frequently in various oil-gas provinces, including that of the Dnepro-Donets valley. Prospects for finding new hydrocarbon catch-basins in this region are tied to tectonic and lithological screening of catch-basins, normally related to relatively monoclinical structures. Isolating and tracing low amplitude disruptions in a sedimentary mantle often becomes ambiguous, although the dependability of tracings of such zones may be increased with special algorithms employing independent gravimetric and magnetometric data. In the present work information on fracture systems in the crystal foundation was used to locate and trace outcropping lines of individual lithological stratigraphic variances in a sedimentary mantle to predict lithological screening of hydrocarbon catch-basins. It is recommended that more dependable tracings of fractures may be obtained by using special types of transformations, such as evaluation of instantaneous coherence of overlapping seismic lines, and frequency filtration of gravimetric fields. Figures 3; references 6 (Russian).

UDC 662.231.21

Use of Heat-Stimulated Discharge To Determine the Parameters of the Thermal Dissociation of Nitrocellulose

907M0314A Moscow KHIMICHESKAYA FIZIKA in Russian Vol 9 No 5, May 90 pp 644-647

[Article by D.M. Zakharenko, Siberian Technological Institute, Krasnoyarsk]

[Abstract] A study of the possibility of using a heat-stimulated discharge without preliminary polarization of samples in an electric field to evaluate some parameters of the thermal dissociation of nitrocellulose, plasticized by glycerine trinitrate, was described and discussed. The study confirmed the possibility of producing polarized films of nitrocellulose without the use of an external electric field. A mechanism of heat-stimulated discharge in polarized films of nitrocellulose was proposed and discussed. Experimental curves of discharge heat flow provided a means of calculating the activation energy and a pre-exponential factor of the first stage of the thermal dissociation of nitrocellulose. The study showed

the possibility of the use of the heat-stimulated discharge method to determine reactions occurring during the thermal dissociation of nitrates of cellulose and analogous substances. Figures 3; references 5: 4 Russian; 1 Western

UDC 536.46

Ignition at the Time of Prechamber Discharge Under Conditions of Turbulence Damping

907M0314B Moscow KHIMICHESKIYA FIZIKA in Russian Vol 9 No 5, May 90 pp 668-672

[Article by I.G. Dik and V.G. Prokofyev; Tomsk State University imeni V.V. Kuybyshev]

[Abstract] A study examined the ignition of a high-temperature turbulent region formed by prechamber emission. A model problem related to this topic was solved. Some assumptions based on experimental observations and theoretical assumptions simplifying the problem were formulated. A study of the problem within the framework of the model compiled showed the existence of some critical conditions of ignition. The irregularity of the distribution of turbulence conditions within the focus degenerated after a time that turned out to be much less than the time of ignition. The damping of the turbulence within the initial time interval, i.e., $\Delta t \approx 10t_{\text{ign}}$, was determined primarily by the expansion of the mixing layer and then by the dissipation of the turbulence energy. Figures 3; references 10 (Russian).

UDC 536.46+541.126

Effect of a Change in the Composition of Detonation Products on the Speed of Throwing a Plate

907M0314C Moscow KHIMICHESKAYA FIZIKA in Russian Vol 9 No 5, May 90 pp 673-680

[Article by S.A. Gubin, V.V. Odintsov, V.I. Pepekin, and V.A. Shargatov, Institute of Chemical Physics imeni N.N. Semenov, USSR Academy of Sciences, Moscow]

[Abstract] This study examines the effect of a change in the composition of detonation products in a scattering process on the velocity of the cast body used. A problem concerning the end-throwing of a plate by exploding a charge of condensed explosive is presented as an example. The process of casting a plate by detonation of a condensed explosive charge is used as a model of the chemical equilibrium of a mixture of the products. A model with a constant composition is also presented. The change in the composition of products during the process of expansion could be ignored in the case of explosions of elemental composition CHNO and CNO containing oxygen in an amount sufficient for complete oxidation of the products. The greatest difference in results of calculations concerning these two models was found for fluorine-containing explosives. The difference

in calculated values of the rate of casting of a plate for explosives of elemental composition CHNO increased with the increase of the fraction of total mass of condensed carbon in the products. The change of composition of products during divergence must be considered because it may have a greater effect on the kinetic energy of the plate at later stages of acceleration than does correct consideration of the physical properties of the material of the plate or splinter phenomena. Figures 4; references 13; 9 Russian; 4 Western.

UDC 536.4

Effect of the Depletion of Inclusions in Filled Polymers in the Preignition Period

907M0314D Moscow *KHIMICHESKAYA FIZIKA*
in Russian Vol 9 No 5, May 90 pp 681-685

[Article by S.Ye. Selivanov and A.A. Shiyon, Kharkov Construction Engineering Institute]

[Abstract] This article describes the derivation of comparatively simple methods and means of describing some elementary processes occurring in filled polymers in the preignition period. An equation for evolution of the radius of inclusions with consideration of the new stationary state (exhaustion) is used. The present technology used to produce filled polymers is based on the use of powders that are close to monodisperse powders. Changes in the surrounding conditions (increase of temperature in the preignition period) caused partial dissolution of the filler and limitation of the rate of dissolution by a diffusion mechanism. In a diffusion regimen, the intensity of destruction of inclusions could be determined by the rate of change of their average radius with time. Relationships were obtained that make it possible (for a broad class of substances of the matrix and the filler) to predict the change in the component composition of the polymer and to thus calculate the key parameters of the kinetics of ignition and combustion. Results obtained in the study may be used to describe the heat-stimulated dynamics of a wide class of binary

polymers in which one of the components is a polymer matrix and the other is a filler in disperse form. Use of the relationships obtained permitted a prediction of the change of the component composition of the polymer and maximum rates of heating at which the thermodynamic equilibrium concentrations of the components of a binary polymer may be used to find ignition parameters. It was also concluded that as the temperature rises on account of an increase in the diffusion coefficient, the rate of dissolution of the inclusions also increases. Figures 2; references 4 (Russian).

UDC 533.6.011.72+533.9.03

Infrared Radiation Behind a Shock Wave With Slightly Ionized Carbon Dioxide Plasma

907M0314E Moscow *KHIMICHESKAYA FIZIKA*
in Russian Vol 9 No 5, May 90 pp 717-720

[S.A. Bystrov, I.S. Zaslonko, Yu.K. Mukoseyev, and F.V. Shugayev, Moscow State University imeni M.V. Lomonosov]

[Abstract] An experimental study of the passage of shock waves through nonequilibrium carbon dioxide plasma, which may involve energy liberation, was described and discussed. Characteristics of the medium behind the shock wave were determined in the plasma by infrared radiation in a wide range of velocities of incoming shock waves. The radiation at a wavelength of 2.7 μm behind the plane shock wave was measured. A high-frequency discharge in the working section of a shock tube created the plasma. The wave itself and the flow behind it maintained their stability during propagation of the shock wave through the region of oscillatory nonequilibrium high-frequency discharge in the power interval considered. Experimental values of luminescence intensity behind the wave were one order of magnitude higher than the theoretically calculated values of equilibrium radiation. This discrepancy was tentatively attributed to the excitation of oscillatory degrees of freedom caused by the passage of an electric current behind the shock wave front. Figures 2; references 7; 5 Russian; 2 Western.

UDC 541.135

Investigation of the Electrochemical Synthesis of Powders of a Mix of Iron, Nickel, and Zinc Hydroxides

917M0019B Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 4, Jul-Aug 90 (manuscript received 2 Feb 90) pp 37-40

[Article by K.K. Lepesov and T.A. Kurdyumova, Institute of Organic Catalysis and Electrochemistry, KazSSR Academy of Sciences]

[Abstract] One of the main problems entailed in producing ferrites with reproducible properties and high magnetic susceptibility is that of producing a metal oxide mix with a high degree of purity and dispersability. The method of chemically precipitating hydroxides and subsequently breaking them down into oxides results in high-quality ferrites. But this method is flawed by the fact that the adsorption capture of impurities (especially Na^+ ions) from the solution by the precipitate results in a high consumption of distilled water when the precipitate is rinsed. Using electrolysis makes it possible to increase the product's purity and homogeneity and to reduce the laboriousness of the rinsing. The most complicated stage in electrochemical synthesis is that of precipitation of a mixture of hydroxides with the specified make-up. In the study reported here, the authors examined the conditions of producing a mix of hydroxides of iron, nickel, and zinc over a wide component concentration range by the electrochemical synthesis method. Using a mixture of Fe_2O_3 , NiO , and ZnO with a mass percent ratio of 62.9:22.9:14.2, they studied the dependence of the solution's pH level on the make-up of the electrolyte and the electrode material. They used a rotating nickel wafer as the cathode (surface = 10 cm^2), a current of 1.5 A, and a temperature of 20°C . The pH level was measured by a pH 340 universal ionometer. The iron and nickel contents were determined spectrophotometrically, and the zinc content was determined by the volumetric method with trilon B. It was discovered that producing a mixture of Fe, Ni, and Zn hydroxides conforming to grade 3048 charge (i.e., a charge with the aforementioned mass percentage ratio) required adding the following to 100 ml of a 1 M solution of NH_4Cl : 0.001 mol $\text{Ni}(\text{NO}_3)_2$; 0.0044 mol $\text{Fe}(\text{NO}_3)_3$; and 0.0033 mol $\text{Zn}(\text{NO}_3)_2$. An electrolysis time of 25 minutes was required with a current of 1 A. The powders produced by the electrochemical method had a dispersability that was a factor of 2.5 higher than that of powders produced by the chemical precipitation method. The following are the magnetic parameters that were measured at a frequency of 1.6 mHz: α , 0.5 μH ; loss angle, $1^\circ = 85^\circ$. Figures 2, table 1; references 8: 7 Russian, 1 Western.

UDC 541.138:621.319.45

Electrochemical Behavior of $\text{Ag-H}_2\text{SO}_4\text{-Ta}_2\text{O}_5$ and $\text{Cu-H}_2\text{SO}_4\text{-Ta}_2\text{O}_5$ Systems During Different Conditions of Polarization

917M0030E Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNLOGIYA in Russian Vol 33, No 9, Sep 90 (manuscript received 8 Dec 89) pp 65-71

[Article by Ye.P. Grishina, D.V. Yermenko, L.N. Tsyplakova, V.N. Kyrov and O.I. Nevskiy, Department of Electrochemical Production Technology, Ivanovo Chemical Technological Institute SKB at the "Elekond" Plant]

[Abstract] A comparative analysis of electrochemical behavior of silver (Sr999) and oxide-free copper (M_{ob}) was carried out under simple working conditions of a tantalum electrolytic condenser (TEC), during the charge-discharge step in absence of a polarizing voltage. The condenser used had a porous Ta_2O_5 anode and flat silver and copper cathodes; the electrolyte consisted of 38% sulfuric acid. It was shown that both metals behaved similarly during the discharge of the condenser and both could be subjected to electrochemical solution enriching the working electrolyte with respective cations. In case of the silver cathode dendritic silver precipitate could form under normal operational conditions which affected the TEC operation in a negative way; this does not happen with copper cathodes. Long term evaluation of TEC showed that copper can be used in place of silver and in a number of cases was even more advantageous. Figures 4; references 22: 19 Russian (6 by Western authors), 3 Western.

UDC 621.357.8

Theoretical and Applied Aspects of Preparation of Aqueous Organic Electrolytes for Electrochemical Processing at Small Inter-electrode Gaps

917M0030F Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNLOGIYA in Russian Vol 33, No 9, Sep 90 (manuscript received 27 Feb 90) pp 77-80

[Article by O.I. Nevskiy, O.K. Zhokhova and V.M. Burkov, Department of Electrochemical Production Technology, Ivanovo Chemical-Technological Institute]

[Abstract] It was shown that using aqueous-organic electrolytes makes it possible to improve the quality of the surface being processed. It was discovered that heat evolution during electrochemical processing (ECP) plays an important role on the end products. A series of requirements was formulated for optimal performance of ECP at small inter-electrode gaps (IEG): 1) electric conductivity of aqueous-organic electrolyte should be

equivalent to that of traditional aqueous electrolytes, which is possible when the organic component can form mobile cations or anions in solutions during their respective chemical reactions; 2) during polarization it is necessary to form a dual layer film in the zone near the electrodes (the phase layer and the viscous layer near the electrode) which, however, would not cause intensive heat evolution; and 3) temperature coefficient of the activation of ionic conductivity of the film should be relatively low. Figure 1; references: 7 (Russian).

UDC [621.9.047:546.831+546.74]:541.135.22

Effect of Composition of Aqueous-Alcoholic Chloride Containing Solutions on Parameters of High Rate Anode Solution of Zirconium and Nickel

917M0030G Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNLOGIYA in Russian Vol 33, No 9, Sep 90 (manuscript received 27 Feb 90) pp 81-84

[Article by A.V. Balmasov, S.A. Lilin and Ye.M. Rumyantsev, Laboratory No 1-14, Institute of Chemistry of Non-aqueous Solutions, USSR Academy of Sciences, Ivanovo Chemical-Technological Institute]

[Abstract] The goal of this work was to investigate the effect of the concentration of n-propyl alcohol, isopropyl alcohol, ethylene glycol and glycerol on the localizing ability of aqueous alcoholic sodium chloride solutions and on the surface coarseness of zirconium and nickel during high rate anode solution. With the exception of glycerol, their logarithmic index of diffusion, which characterizes the localizing properties of the electrolytes, depended mostly on the concentration of sodium chloride and not on the alcohol. The quality of the treated surface depended on the nature and concentration of the components of the solution and on the inter-electrode gap. Evidently, this is due to the formation of a viscous layer close to the electrode which is saturated with zirconium solution products. References 6: 5 Russian, 1 Western.

UDC 541.138.3

Application of Computers to Studies of Electrode Processes Kinetics

917M0030H Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNLOGIYA in Russian Vol 33, No 9, Sep 90 (manuscript received 7 May 90) pp 85-88

[Article by V.V. Opekhova, V.M. Artemenko and V.P. Gomofov, Department of Electrochemical Processes Technology, Kharkov Polytechnical Institute]

[Abstract] One of the most popular methods for investigating kinetics of electrode processes is the analysis of the polarization curves. The treatment of polarization curves is simplified considerably by the use of computer technology. A program was proposed for processing the polarization curves in the coordinates of electrochemical, diffusion and mixed kinetics. The program was written in the BASIC language for the computer "Elektronika BK 0010-10". An example was given in which this program was used to process cathode polarization curves obtained in solutions in which the cathode process was not accompanied by a slowed down chemical and physical phases. Figures 2; references: 1 (Russian).

UDC 621.9.047

Electrochemical Solution of Chromium in Formamide Solutions of NaClO₄

917M0030I Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNLOGIYA in Russian Vol 33, No 9, Sep 90 (manuscript received 15 May 90) pp 89-91

[Article by G.F. Shpak, A.V. Maslov and B.P. Saushkin, Department of Machine Construction Technology, Kishinev Polytechnical Institute imeni S. Lazo]

[Abstract] In an attempt to explain the nature of the limiting phase of the ionization of chromium in a formamide solution, the effect of hydrodynamics, salt concentration, temperature of the solution and the rate of potential development on the magnitude of the limiting current was investigated using potential-dynamic and -static methods. It was concluded that diffusion was the rate limiting step in the electro-oxidation process. In formamide chloride media the anode solution process is controlled by the electrolysis products removal from the phase separation border into the solution. Figures 3; references: 3 (Russian).

UDC 669.245:536.425

Phase Transformation Characteristics in Ni₃Fe Powder Alloy

917M0018G Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV, No 5, Sep-Oct 90 (manuscript received 25 Apr 89) pp 132-136

[Article by A.A. Nuzhdin, Moscow]

[Abstract] The ordering process in sintered powder alloy Ni₃Fe was studied at room temperature and at elevated levels. The porosity of powdered Ni₃ of transition to the nonordered state depends on the heating rate: an increased heating rate shifts this threshold toward lower temperatures. A major role of the thermal stress in these specimens in respect to the changes in electric resistance of the porous bodies was assumed. In the temperature range of the low-temperature phase, the coefficient of thermal expansion did not depend on the porosity of the alloy; during the phase transition the coefficient of thermal expansion increased. The nonordered state of Ni₃Fe showed a somewhat lower volume modulus. Figures 4; references: 7 (Russian, 1 by Western authors).

UDC 541.451

Porous Structure of Titanium Dioxide

917M0020F Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 56 No 9, Sep 90 (manuscript received 24 Aug 89) pp 998-1001

[Article by V.V. Shimanovskaya, A.M. Puziy, I.T. Chashechnikova, and V.V. Strelko, Sorption Division, Institute of General and Inorganic Chemistry, UkSSR Academy of Sciences, Kiev]

[Abstract] This article reports experimental results regarding the formation of the porous structure of TiO₂ samples obtained by thermal hydrolysis of titanium tetrachloride solutions in the presence of titanium hydrochloride with anatase or rutile structures. It was shown that the pore structure of anatase and rutile was different and depended on the conditions of hydrolysis and thermal treatment. Annealing of the product in a stream of oxygen accelerated the baking process and the ensuing changes in the porous structure of TiO₂: the total pore volume and effective mesopore radius were decreased, while the apparent density and effective radius of the macropores increased. In the mixed composition material containing both the anatase and rutile, the most developed porosity was found in the samples consisting of 70% rutile and 30% anatase. Figure 1; references 10: 9 Russian, 1 Western.

UDC 543.422:541.183

Electron Acceptor Properties of the Surface of Amorphous Gallium Aluminosilicates

917M0026A Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 64 No 10, Oct 90 (manuscript received 13 Jul 89) pp 2730-2735

[Article by Ye.V. Lunina, A.D. Motina, and G.L. Markaryan, Chemistry Department, Moscow State University imeni M.V. Lomonosov]

[Abstract] The problem of determining the nature of the electron acceptor centers on the surface of multicomponent catalysts is a complex research task. Conventional research methods such as IR spectroscopy of adsorbed pyridine do not permit confident differentiation of electron acceptor centers with different natures or precise determination of their concentrations. The paramagnetic probe method is more useful in this respect. The authors of the study reported herein used the paramagnetic probe method to study the formation of the coordination-unsaturated states of the cations Al³⁺ and Ga³⁺ on the surface of gallium aluminosilicates with different make-ups. They demonstrate that applying small quantities of gallium ions onto the surface of aluminosilicate leads to an anomalous increase in the concentration of coordination-unsaturated aluminum ions on the surface of the test specimens and that when this is done no gallium ions can be detected. It is also established that Ga³⁺ coordination-unsaturated ions appear when the Ga/Al ratio reaches 0.1 or more and that their concentration increases as the amount of aluminum atoms decrease. It is hypothesized that the changes observed are due to isomorphic substitution in the system Ga₂O₃-Al₂O₃-SiO₂, hence the conclusion that applying cations of elements capable of isomorphic substitution to the surface of aluminosilicates triggers complex processes resulting in nonadditive changes in the surface's acid properties. Figures 4; references 10: 8 Russian, 2 Western.

UDC 541.128

Activation of Silicon Oxide Films by Heteropoly Compounds

917M0026B Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 64 No 10, Oct 90 (manuscript received 8 Sep 89) pp 2736-2740

[Article by S.A. Krutovertsev, O.A. Subocheva, G.A. Grigoryev, S.I. Sorokin, and O.D. Menshikov]

[Abstract] Because the reaction of the vapors of low-molecular weight compounds with oxide films results in a significant change in the electrophysical properties, oxide films have been used as the sensitive layers of sensors detecting the make-up of gas. Silicon oxide films activated by such additives as P₂O₅ and LiCl have been used for this purpose; however, because such systems are

used primarily in moisture sensors, their capabilities are significantly limited. Attempts have therefore been made to find other activators based on catalytic oxidation. In a continuation of this line of research, the authors of the study reported herein examined the activation of silicon oxide films by heteropoly compounds. By using the method of hydrolytic polycondensation of solutions based on tetraethoxysilane as described elsewhere, they produced silicon oxide films containing heteropoly compounds. They studied the processes of the adsorption of hydrazine vapors on films subjected to different heat treatments at temperatures ranging from 370 to 1,000 K. They demonstrated that the structure of the heteropoly compound can be preserved in the silicon oxide films to which they are added by selecting the optimum heat treatment regimen. They further established that chemisorption occurs when films are heat-treated to 383 K. In the case of heat treatment at 523 K or above, the heteropoly compounds undergo a significant change in their properties; this leads to a change in the nature of their films' adsorption. The chemical reaction of heteropoly compounds with hydrazine is demonstrated to be accompanied by a change in the electric conduction of the resultant film. It is thus concluded that they can be used as the basis for producing sensors to monitor the concentration of active gases and vapors. Figures 3; references 19: 17 Russian, 2 Western.

UDC
532.74+534.231+546.241'(289+811+815)+53.072:681.3

Modeling the Temperature Dependence of the Propagation Rate of Ultrasound in Melts of the Compounds GeTe, SnTe, and PbTe Based on the Theory of Associative Equilibria

917M0026C Moscow *ZHURNAL FIZICHESKOY KHIMII* in Russian Vol 64 No 10, Oct 90 (manuscript received 15 Jan 90) pp 2852-2856

[Article by V.M. Glazov and A.V. Shishkin, Moscow Electronics Technology Institute]

[Abstract] In their earlier research, the authors of the study reported herein demonstrated that the theory of associative equilibria is a universal means of describing the entire set of thermodynamic and structural characteristics of systems with a strong chemical reaction. Because additional research showed that the thermodynamic and structural properties of GeTe, SnTe, and PbTe melts are well described by the theory of associative equilibria, the authors decided to illustrate the capabilities of the associative equilibria approach by way of the example of modeling the temperature dependence of the propagation of ultrasound in melts of these compounds. To do so, they performed a series of calculations based on the theory of associative equilibria and compared their results with published results of experiments on the same topic. They found their results to be in good agreement with the data obtained in actual experiments. They were thus able to conclude that in the

case of a GeTe melt, as the temperature increases, there is a restructuring of the close-order structure that is connected with the occurrence of three reactions: $\text{Te} + \text{Te} \rightarrow \text{Te}_2$, $\text{Ge} + \text{Te} \rightarrow \text{GeTe}_2$, and $\text{Ge} + \text{Te} \rightarrow \text{GeTe}$. These processes encompass a large temperature interval. The effect noted is significantly reduced in an SnTe melt on account of the reduction in the amount of Te-Te bonds formed as the temperature increases, and the effect completely disappears in a PbTe melt, where the reaction $\text{Pb} + \text{Te} \rightarrow \text{PbTe}$ at the given temperatures is characterized by the greatest association constant. In other words, it is the reduction in the contribution of the Te-Te bond that above all determines the difference in the temperature dependence of the rate of ultrasound propagation in GeTe, SnTe, and PbTe melts. The results obtained confirm the great promise of using the theory of associative equilibria to describe and explain structure-sensitive characteristics in melts with a strong chemical reaction. Figure 1; references 20: 13 Russian, 7 Western.

UDC 66.087.7:546.711:546.76:620.187

Electron Microscopy Study of the Surface of Coatings Made of the Alloy Mn-Cr

917M0028A Vilnius *LIETUVOS MA. CHEMIJA* in Russian No 4, Apr-May-Jun 90 (manuscript received 24 Oct 89) pp 3-10

[Article by T. Bernatavichyus, E. Vitkene, and V. Skominas, Chemistry and Chemical Technology Institute, LiSSR Academy of Sciences]

[Abstract] A study examined the morphology of the surface of coatings of the alloy Mn-Cr that were produced in an electrolyte containing glycine or ammonium ions and different concentrations of selenate. The test coatings were electrodeposited in two electrolytes. The first contained the following (in g/l): $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$, 100 (sometimes 200); $\text{NH}_2\text{CH}_2\text{COOH}$, 20; $\text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O}$, 0.5 to 8; and Cr^{3+} , 1 to 3 with $i_k = 2$ and 10 A/dm². The second electrolyte contained the following (also in g/l): $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$, 100; Cr^{3+} , 1 to 3; $(\text{NH}_4)_2\text{SO}_4$, 125; and $\text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O}$, 0.5 to 8 with $i_k = 10$ and 20 A/dm² (in some experiments, 40). The coatings were deposited onto copper foil about 10 μm thick at a temperature of 20°C. The resultant coatings were then subjected to electron microscopy studies. It was concluded that the electrocrystallization of coatings of the alloy Mn-Cr is determined primarily by processes connected with the codeposition of Se. Smooth and very fine crystalline coatings with an Se content of about 0.5% were deposited. Their formation was not affected by the Cu defects in the substrate. Electrocrystallization of coatings containing about 1% Se occurred mainly in the defective sections of the substrate. Figures 5; references 2 (Russian).

UDC 678.673.41.5

The Effect of Polycarbonate Fillers on the Adhesion of a Cu Coating

917M0028B Vilnius LIETUVOS MA. CHEMIJA
in Russian No 4, Apr-May-Jun 90 (manuscript received
5 May 89) pp 11-17

[Article by L. Daukshayte and Y. Vinkyavichyus, Chemistry and Chemical Technology Institute, LiSSR Academy of Sciences]

[Abstract] The study reported herein examined the effect of polycarbonate fillers on the adhesion of Cu coatings. The effects that PK-3 polycarbonate without any filler, with a TiO_2 filler, and with TiO_2 and AlN fillers had on the adhesion of Cu coatings on surfaces made of these polycarbonates were compared. During the experiments, wafers (50 x 20 x 2 mm) were first treated in a 93% solution of dimethylformamide at a temperature of 40°C for 3 minutes, rinsed in isopropyl alcohol, and then etched in a chromium mixture consisting of 380 g/l H_2SO_4 and 400 g/l CrO_3 at 60°C. The wafers were then sensitized and activated in accordance with the classic method. A Wein solution was used for the chemical copper plating (temperature, 20°C; pH, 12.6; and charge density, 2 dm^2/l). A JXA-50A scanning electron microscope was used to examine the coatings. It was discovered that a TiO_2 filler does not affect the extent of adhesion, whereas an AlN filler strongly increases the adhesion of polycarbonate when it is treated in dimethylformamide and then in isopropyl alcohol and then subsequently etched in a mixture of H_2SO_4 and CrO_3 . It was hypothesized that, along with the contribution that mechanical bonds make to adhesion, the formation of chemical or physicochemical bonds between the AlN fillers and the coating or the interphase Cu oxides also exert a strong effect on the degree of adhesion achieved. Figures 4; references 2 (Russian).

UDC 678.673.41.5:539.612:546.222

Effect of Polycarbonate Fillers on the Adhesion of Cu_{2-x}S Coating

917M0028C Vilnius LIETUVOS MA. CHEMIJA
in Russian No 4, Apr-May-Jun 90 (manuscript received
4 May 89) pp 18-22

[Article by Y. Vinkyavichyus and L. Daukshayte, Chemistry and Chemical Technology Institute, LiSSR Academy of Sciences]

[Abstract] The authors of the study reported herein compared the adhesion of Cu_{2-x}S coatings to polycarbonates with and without fillers. In their experiments, they used the following: PK-3 polycarbonate without any filler; polycarbonate with a TiO_2 filler; and polycarbonate with TiO_2 , AlN, and polypropylene. They formed electroconductive layers of Cu_{2-x}S onto prepared polycarbonate bases measuring 20 x 20 x 2 mm in accordance

with procedures detailed elsewhere. The amount of S sorbed on the polycarbonate surface in sulfide was determined by the radioactive indicator method using ^{35}S . A JXA-50A electron microscope was used for the Cu electron microscopy studies performed. It was discovered that the adhesion of a Cu_{2-x}S coating to a polycarbonate surface increases sharply (by 2 to 3 kN/m) in the presence of an AlN filler, thus exceeding the adhesion of a Cu coating by a factor of 1.5 to 2.0. The Cu_{2-x}S content on the polycarbonate surface also increases sharply in the presence of an AlN filler (by a factor of 6 to 8). The positive effect of AlN on the adhesion of Cu_{2-x}S to polycarbonate was attributed to the formation of chemical or other bonds. Figures 4; references 9 (Russian).

UDC 628.38

Magnetic Materials Based on Technical-Grade Fe-Ni-Co Ferrites From Electroplating Waste Water Sludge

917M0028D Vilnius LIETUVOS MA. CHEMIJA
in Russian No 4, Apr-May-Jun 90 (manuscript received
23 Nov 89) pp 52-56

[Article by M. Ptashkas, I. Stepanchikova, S. Makarov, Yu. Budilovskiy, and V. Zaytsev, Litstankoproyekt Scientific Production Association]

[Abstract] Electroplating waste water sludge from the Panevezhis Precision Mechanics Plant was used as a source for producing prototype magnetic materials based on technical-grade Fe-Ni-Co ferrites. The existing method of preparing ferrites was used as the basis for manufacturing the prototypes. Tests were performed to determine the main physicomachanical and magnetic properties of the prototype specimens developed. These tests revealed the presence of nickel and cobalt ferrites along with barium hexaferrite. It was determined that barium hexaferrite with a stoichiometric make-up constitutes the test specimens' main crystalline phases. The ferrites produced did not differ from one another from the standpoint of physicomachanical properties. It was discovered, however, that adding cobalt-containing sludge increased the specimens' coercive force. Cobalt-containing electroplating sludge was thus deemed suitable for use in producing magnetic materials with high magnetic characteristics. The ferrites developed at the Panevezhis Precision Mechanics Plant were compared with ferrites that were produced from waste water sludge at the Moscow Chemical Technology Institute imeni D.I. Mendeleev. The two groups of ferrites had identical compression strengths and densities; the ferrites produced at the plant in Panevezhis had a high coercive force (800-1,000 versus 600-800 oersteds) and a higher abrasability (2-3 versus 1.5-2%). Figures 2, table 1; references 10: 5 Russian, 5 Western.

UDC 541.128.13:546.271.94

Catalytic Oxidation of BH_4^- on Osmium

917M0028E Vilnius LIETUVOS MA. CHEMIJA
in Russian No 4, Apr-May-Jun 90 (manuscript received
20 Oct 89) pp 67-71

[Article by Ya. Valsyunene, G. Kaykaris, and V. Drunga.
Chemistry and Chemical Technology Institute, LiSSr
Academy of Sciences]

[Abstract] The authors of the study reported herein
undertook the task of deriving quantitative characteristics
of the catalytic activity of osmium in the reaction of
 BH_4^- with water and to develop a greater understanding

of the mechanisms of the reaction. They used the volumetric method to examine the said reaction and produced the catalyst used in the experiments (i.e., metallic osmium powder) by mixing aqueous solutions of NaBH_4^- with OsO_4 . They reacted the BH_4^- (between 0.006 and 0.28 mol/l) in alkaline solutions on osmium powder ($S = 10 \text{ m}^2/\text{g}$) in the temperature interval from 50 to 90°C . The rate of the process was found to depend on the temperature, initial concentration of BH_4^- , and the quantities of catalyst and alkaline solution used. The average conventional activation energy of the process was found to equal 28.9 kJ/mol. The authors propose an empirical equation to describe an actual BH_4^- process and present the values of its coefficients as determined from the experiment results by using the least squares method. Figures 4, tables 2; references 7 (Russian).

UDC 621.315.55.592.539.216.2

Formation Characteristics of TiSi_2 on Polycrystalline Silicon

917M0018E Moscow *FIZIKA I KHIMIYA OBRABOTKI MATERIALOV* in Russian No 5, Sep-Oct 90 (manuscript received 29 May 89) pp 97-102

[Article by O.B. Yatsenko, V.Ye. Niskov, L.Ya. Tverdokhlebova, and E.V. Sklyarova, Voronezh]

[Abstract] Characteristics of the formation of TiSi_2 on polysilicon were investigated during stationary thermal annealing of titanium plates in a vacuum; the effect of As and B dopants was analyzed along with their redistribution during silicide formation. It was established that the growth rate of TiSi_2 in the thin-layer structure of titanium-polysilicon depended on the admixture implanted in the polysilicon by the ionic implantation. Extensive alloying of polysilicon with arsenic slowed down the silicide formation process, which could result in an incomplete transition of titanium film into the silicide and cause thinner TiSi_2 films. During high-temperature annealing, the probability of morphologic degradation of such layers increased significantly. The ion-implanted boron showed no significant effect on the growth of TiSi_2 . Yet, during this process it too is redistributed from the polysilicon into the silicide and even toward its surface. This depletes the silicide-polysilicon junction of the alloying mixture. Figures 4; references 6: 1 Russian, 5 Western

UDC 669.018.95

Composites Produced by Deposition From the Vapor Phase in Vacuum

917M0018F Moscow *FIZIKA I KHIMIYA OBRABOTKI MATERIALOV* in Russian No 5, Sep-Oct 90 (manuscript received 8 Aug 89) pp 108-117

[Article by B. A. Movchan, Kiev]

[Abstract] The technology and advantages of producing composites by deposition from the vapor phase in a vacuum have been reviewed, accenting the developments worked out at the Institute of Electric Welding (Imeni Ye.O. Paton at the UkSSR Academy of Sciences. The processes of electron beam evaporation of metals and nonmetals followed by condensation of the vapor phase make it possible to control the structure of large condensed units. The structures and mechanical behavior of two classes were reviewed: microlayered and dispersion-hardened objects; in addition, the commercial electron beam equipment for production of such objects was discussed. The process is practical and economical and yields long-lasting, reliable machine components with novel performance capabilities. Applications are found in ceramic covers of turbine blades, in the preparation of thick-layer construction covers, in various tools and dies with complex shapes that have to

by made of material difficult to process, and in the production of novel intermediate materials for further processing, like Cu-Mo, Pt-ZrO₂, Cr-Al₂O₃, TiC, SiC, etc. Figures 7, references 25: 14 Russian (2 by Western authors), 11 Western (2 by Russian authors).

UDC 542.49+536.45

Thermodynamic Functions of $\text{YBa}_2\text{Cu}_3\text{O}_7$, $\text{YBa}_2\text{Cu}_3\text{O}_6$, Y_2BaCuO_5 , and BaCuO_2

917M0026D Moscow *ZHURNAL FIZICHESKOY KHIMII* in Russian Vol 64 No 10, Oct 90 (manuscript received 12 Jul 89) pp 2606-2610

[Article by D.Sh. Tsagareyshvili, G.G. Gvelesiani, I.B. Baratashvili, G.K. Moiseyev, and N.A. Vatolin]

[Abstract] Computer thermodynamic modeling of the formation of high-temperature superconductive metal oxide phases and related metal oxide compounds requires the creation of a bank of experimental and calculated data on these compounds' thermodynamic properties. Because the existing experimental values of these constants are sorely lacking, the authors of this article undertook the task of calculating the main thermodynamic properties of the phases $\text{YBa}_2\text{Cu}_3\text{O}_7$, $\text{YBa}_2\text{Cu}_3\text{O}_6$, Y_2BaCuO_5 , and BaCuO_2 . They did so by using existing empirical and semiempirical relationships as well as their own original empirical and semiempirical relationships. In this article they present their calculated values of the following for each of the aforementioned compounds: standard enthalpy of formation, standard entropy, enthalpy increment and standard heat capacity, temperature dependence of the heat capacity in the temperature interval from 298 K to the melting point, heat and entropy of melting, and heat capacity in the liquid state. Tables 2; references 16: 10 Russian, 6 Western.

UDC 543.42.062:547.419.1

The Accelerating Effect of Organophosphorus Compounds and Aldehydes in the Reaction of the Oxidation of Aromatic Amines by Hydrogen Peroxide

917M0027D Moscow *VESTNIK MOSKOVSKOGO UNIVERSITETA* in Russian Vol 31 No 5, Sep-Oct 90 (manuscript received 5 Jul 89) pp 500-507

[Article by I.F. Dolmanova, G.A. Zolotova, and I.Yu. Kharitonova, Analytic Chemistry Department, Moscow University]

[Abstract] Researchers have described a catalytic method of determining acylating phosphorus (V) derivatives on the basis of their accelerating effect in the oxidation of aromatic amines by hydrogen peroxide in an alkaline water and acetone medium. Others have hypothesized that aldehyde is oxidized by hydrogen

peroxide to α -oxyhydroperoxide, which in turn decomposes rapidly and forms radicals oxidizing n-phenylenediamine to their end product, i.e., a Bandrowski base. The authors of the study reported herein explored the question of whether the types of reactions constituting the basis of methods of determining organophosphorus compounds and aldehydes are of the same type and whether the mechanisms of their accelerating effect are identical. First, they reacted o-dianizidine with hydrogen peroxide in the presence and absence of triphenylphosphate. Next, they examined the reaction of the oxidation of n-phenylenediamine with hydrogen peroxide with and without the presence of benzaldehyde. They also examined the effect of the combined presence of triphenylphosphate and benzaldehyde. (The procedures used to prepare the test compounds and conduct both reactions are detailed.) They examined the effect of the pH level of the medium and nature of the buffer solution, the nature of the solvent, and the nature of the reducing agent on the mechanism of the reactions examined. The resultant data indicated that the reactions of the oxidation of aromatic amines by hydrogen peroxide in the presence of organophosphorus compounds and aldehydes proceed by different catalytic effect mechanisms. This made it possible for the authors to clarify the interfering effect of organophosphorus compounds and aldehydes when they are determined by the type of indicator reaction examined and to make a directed selection of systems for using the catalytic method to determine the organic compounds researched. Figures 2, table 1; references 4: 2 Russian, 2 Western.

UDC 541.123.3:546.34.35.656

Phase Equilibria in LiCl-RbCl-PrCl₃ System

917M0030J Ivanov IZVESTIYA VYSSHIKH UCHEBNIKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA in Russian Vol 33, No 9, Sep 90 (manuscript received 24 May 89) pp 121-122

[Article by I.I. Trifonov and T.A. Pobirchenko, Department of Machine Construction Technology, Kovrov Branch of Vladimir Polytechnical Institute]

[Abstract] One of the more important tasks during development of production or refining processes of metals by electrolysis of molten media is the proper selection of the electrolyte. The fusion process of salt compositions containing Li, Rb and Pr chlorides was investigated using the differential-thermal analysis method. Fusion of LiCl-RbCl-PrCl₃ system was evaluated by the method of polythermal sectioning. A quasi-binary section LiCl-3RbCl.PrCl₃ was identified in this system along with two ternary eutectics in the subsystem LiCl-RbCl-3RbCl.PrCl₃ and two peritectic conversions in the subsystem LiCl-3RbCl.PrCl₃-PrCl₃. Figure 1; references: 5 (Russian).

UDC 541.1

Doping Characteristics of HTSC Compounds EuBa₂Cu₃O₇ With Iron Ions

917M0035A Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 35 No 11, Nov 90 (manuscript received 23 Apr 90) pp 2723-2728

[Article by G.A. Chesnokov, V.A. Novichkov, A.A. Stebunov, M.Kh. Sabirov, R.A. Stukan, A.G. Knizhnik and Ye.F. Makarov, Institute of Chemical Physics imeni N. N. Semenov, USSR Academy of Sciences, and Scientific Production Cooperative "Poisk", Moscow]

[Abstract] The effect of synthetic conditions (time and temperature of annealing, composition of the atmosphere and its pressure, extent of the doping with iron ions) used in production of EuBa₂Cu_{3-x}Fe_xO₄ (0 ≤ x ≤ 0.45) on its properties was investigated by mossbauer spectroscopy. Because the production of europium ceramics requires more drastic conditions than production of yttrium ceramics, this could have an effect on the iron doping effectiveness. It was shown that it is necessary to temper the Eu-Ba-Cu-Fe specimen at 915 °C for at least 100 hrs to assure the completion of the formation of iron doped HTSC. The specimens doped with iron bound the oxygen and retained it to a greater extent than the non-doped specimens. In contrast to Y-HTSC, the Eu-HTSC showed a stronger dependence of the temperature of transition into the superconducting state on the degree of the replacement of copper by iron ions. Figures 5; references 10: 4 Russian (1 by Western author), 6 Western.

UDC 546.87.14.21

Bi₂O₃-BiOBr-CuO System Reactions

917M0035B Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 35 No 11, Nov 90 (manuscript received 25 May 90) pp 2729-2731

[Article by O.I. Aleksandrova, L.N. Kholodkovskaya, V.A. Yermeyev, V.A. Dolgikh and B.A. Popovkin]

[Abstract] An attempt was made to synthesize new high temperature superconducting materials based on bismuth oxahalides; the Bi₂O₃-BiOBr-CuO system was investigated, concentrating on BiOBr-CuO, because the other subsystems the BiOBr-Bi₂O₃ and Bi₂O₃-CuO have already been characterized. The authors failed to find any new compounds inside the Bi₂O₃-BiOBr-CuO triangle. An area of solid solutions Bi_{2-x}Cu_xO₂Br_{2-y} (0 ≤ x ≤ 0.5; y ≤ x) was noticed in the BiOBr-CuO system; green monocystals were obtained for x=0.5. All HTSC materials exhibit continuous Cu-O layers with different degree of copper oxidation. The materials obtained in this study did not exhibit this continuity of Cu-O layers and probably this was the reason for the

absence of superconducting property. Figure 1; references 5: 4 Russian, 1 Western.

UDC 54.022:546.161

Structural Properties of Inorganic Fluorides

917M0035C Moscow ZHURNAL
NEORGANICHESKOY KHIMII in Russian Vol 35
No 11, Nov 90 (manuscript received 23 Mar 89)
pp 2758-2765

[Article by V.D. Klimov, Institute of Atomic Energy
imeni I.V. Kurchatov, Moscow]

[Abstract] A review was presented of the structural characteristics of inorganic fluorides. On the basis of their bonds, fluoride compounds can be grouped as follows: ionic fluorides, covalent compounds, fluorides with mixed ionic-covalent bonds and molecular adducts in which intermolecular coulomb attraction predominates. The review covered structural characteristics and molecular forms of the following inorganic fluorides: fluorides with ionic bonds, complex fluorides, graphite fluorides, fluorides with bridge bonding, molecular fluorides and molecular adducts. It was concluded that studies of fluoride structures are of great practical importance because of the wide use of fluoride compounds in science and technology. Figures 9; references 16: 6 Russian (2 by Western authors), 10 Western.

UDC 546.791.18:546.77

Reaction of Titanium and Zirconium With Uranium Monophosphide

917M0035D Moscow ZHURNAL
NEORGANICHESKOY KHIMII in Russian Vol 35
No 11, Nov 90 (manuscript received 3 Jan 90)
pp 2766-2768

[Article by A.S. Panov]

[Abstract] Most of the available reports on the reaction of titanium and zirconium with uranium monophosphide are of descriptive nature; the goal of this study was to investigate reaction kinetics in this system and to establish the nature of the interaction layers. Experiments were carried out at 1073-1473 K with application of the metallographic, microdurometric, x-ray structural and micro x-ray spectral analyses. The reaction products consisted of TiP and ZrP with solid solutions of uranium and phosphorus in the metals. The thickness of the monophosphide layers increased with temperature. Kinetic constants of the growth of monophosphide layers were determined. The growth of phosphide layers on titanium and zirconium should stop when the composition of uranium monophosphide reaches lower limits of phase homogeneity. The maximum possible thickness of TiP and ZrP layers depends

on the initial composition, and the relationship between UP and the metals competing with it. References 11: 1 Russian, 10 Western.

UDC 54-165:537.621.18.02

Magnetic Evaluation of Co^{II} and Ni^{II} Atom Distribution in Solid Solutions $M_xMg_{1-x}Al_2O_4$ With a Spinel Structure

917M0035E Moscow ZHURNAL
NEORGANICHESKOY KHIMII in Russian Vol 35
No 11, Nov 90 (manuscript received 16 Apr 90)
pp 2824-2876

[Article by N.V. Chezhina and N.V. Savelyeva]

[Abstract] A new method was proposed for analysis of the distribution of paramagnetic atoms in non-equivalent spinel structure positions. An attempt was made to show the universal applicability of this method to solving similar tasks and in search for principal tendencies in the distribution of atoms by non-equivalent sub-lattice networks. The nature of exchange interactions during substitution of paramagnetic atoms within the limits of a transition series of the periodic system was elucidated. Specifically, the magnetic susceptibility of solid solutions $M_xMg_{1-x}Al_2O_4$ (M - Co, Ni; $0.005 \leq x \leq 0.15$). Based on the analysis of the magnetic characteristics expressed as functions of concentration and temperature, the fraction of paramagnetic atoms in tetra- and octa- positions of the lattice were determined. It was shown that $\alpha_T(\text{Co}) = 1$, $\alpha_T(\text{Ni}) = 0.86$ and that the degree of spinel inversion of MA_2O_4 increased gradually in the series Co^{II} - Ni^{II} - Cu^{II} . This method was recommended for determination of the degree of inversion based on magnetic susceptibility data of any spinels of solid solutions containing multi-component paramagnetic atoms. Figures 23; references 7: 4 Russian (1 by Western author), 3 Western.

UDC 546.666:(541.49 + 541.67)

Complex Formation of Er³⁺ With Nitrate Ions Based on Data of Magnetic Double Refraction and Nuclear Magnetic Relaxation

917M0035F Moscow ZHURNAL
NEORGANICHESKOY KHIMII in Russian Vol 35
No 11, Nov 90 (manuscript received 27 Mar 90)
pp 2877-2880

[Article by N.V. Utyaganov, S.G. Vulfson, F.V. Devyatov and Yu. I. Salnikov, Odessa State University imeni I.I. Mechnikov]

[Abstract] The linear magnetic double refraction method is an effective procedure for studying the structure and magnetic-electric properties of various paramagnetic complexes. Their molar constant of magnetic double refraction (MD) depends on molecular parameters: anisotropy of magnetic susceptibility and electric polarizability. The MD constant is an additive value based on molecular composition of the system. Magneto-optic and magneto-relaxation properties of a series of aqueous

solutions of Er^{3+} cations (0.13 mole/l) in varying concentration of the nitrate ions (ranging from 0.4 to 6.7 mole/l) were determined. The stoichiometry of external and internal spherical complex particles was determined along with stability constants. Spatial structure of the complex $[\text{Er}(\text{NO}_3)_2(\text{H}_2\text{O})_{n-3}]$ was elucidated. Figures 4; references 8: 6 Russian, 2 Western.

UDC 539.194

Theoretical Investigation of Structural Flexibility, Stability and Reactivity in Fluoride Salt Molecules NF_4BF_4 , NH_4AlF_4 and PF_4BF_4

917M0035G Moscow ZHURNAL

NEORGANICHESKOY KHIMII in Russian Vol 35

No 11, Nov 90 (manuscript received 5 Mar 90)

pp 2899-2905

[Article by L.Ye. Baranov and O.P. Charkin, Institute of Novel Chemical Problems, USSR Academy of Sciences]

[Abstract] Nonempirical investigation of structural flexibility and resistance to the breakdown of complex salt molecules of the type DX_4AY_4 was continued, concentrating on the cation-anion interactions in the NF_4BF_4 , NF_4AlF_4 and PF_4BF_4 salts. Nonempirical calculation SSP with an average base of $3-21 \text{ G} + 3\text{d}(\text{Al,P})$ was carried out for these molecules with partial optimization of their geometry at different mutual orientations of tetrahedral cations and anions. The molecules appeared to be flexible in respect to intramolecular cation and anion rotations with about a 4 kcal rotation barriers. The breakdown energies for DF_4AF_4 yielding $\text{DF}_3 + \text{F}_2 + \text{AF}_3$ and PF_4BF_4 yielding $\text{PF}_5 + \text{BF}_3$ were determined. All of these molecules were unstable. Electrostatic, polarizational and covalent components of the cation-anion interaction energies were discussed. In comparison to hydride cations like NH_4^+ and PH_4^+ , the fluorides NH_4^+ and PF_4^+ were found to be much less polarized. Figures 2; references: 1 (Russian).

UDC 541.15:541.64.547.51.128

**Electron Spectra of Branched Cruciform
Heteroorganic Oligomers With Silicon, Titanium,
Germanium, and Tin Atoms in Their Branching
Center**

917M0027B Moscow VESTNIK MOSKOVSKOGO
UNIVERSITETA in Russian Vol 31 No 5, Sep-Oct 90
(manuscript received 23 Aug 89) pp 491-495

[Article by L.N. Pankratova, M.V. Simakova, and
Ye.Ye. Stepanova, Electrochemistry Department,
Moscow University]

[Abstract] The possibilities of synthesizing spirocyclic heteroorganic polymers depends largely on the reactivity of the end OH groups of the branched cruciform heteroorganic oligomers with silicon, titanium, germanium, and tin atoms at the branching center. Others have researched certain aspects of this topics; however, the literature does not yet contain any information regarding the possibility of the formation of a donor-acceptor complex with charge transfer, in which case the reactivity of the end OH groups would change. Consequently, the authors of the study reported herein examined the electron spectra of branched methylphenylsiloxane oligomers with Si, Ti, Ge, and Sn atoms at the branching center in the initial state and in the form of solutions in polar and nonpolar solvents. In addition to the test compounds, the used the linear organosilicon oligomer PFSM-4 as a control compound. They obtained detailed data regarding the absorption and fluorescence spectra of the test oligomers and the PFSM-4. Analysis of the fluorescence spectra of the oligomer with a Ti atom at the branching center in solutions of either cyclohexane or tetrahydrofuran revealed the formation of stable intramolecular excimers at concentrations below 0.5 mg/mg. No such excimer formation was observed in the case of oligomers with Si, Ge, or Sn atoms at the branching center. It was hypothesized that this difference is connected with the restriction of the mobility of the siloxane chains of the molecule with the Ti atom at the center, which is confirmed by data regarding the formation of a charge carrier complex in the given oligomer. Figures 3, table 1; references 8: 6 Russian, 2 Western.

UDC 542.42

**Determining Zn, Pb, and Ag in Water by the
Atomic Adsorption Method**

917M0027C Moscow VESTNIK MOSKOVSKOGO
UNIVERSITETA in Russian Vol 31 No 5, Sep-Oct 90
(manuscript received 10 Jul 89) pp 513-515

[Article by N.Ye. Kuzmenko, N.V. Golovina, G.V. Kozyreva, V.A. Popkov, and G.D. Brykina, Analytic Chemistry Department, Moscow State University, and Moscow Medical Academy imeni I.M. Sechenov]

[Abstract] The photometric method is most often used to determine inorganic impurities in water. One of its drawbacks is the large amount of time required to prepare samples and eliminating the effect of interfering elements. Because atomic absorption spectroscopy is a more precise, quicker, and more sensitive alternative, the authors of the study reported herein examined the feasibility of using the atomic absorption spectroscopy method to determine zinc, lead, and silver in surface and drinking waters. Direct use of atomic absorption spectroscopy and atomic absorption spectroscopy after sorption concentration were compared. Solutions of lead (1 to 8 µg/ml), zinc (0.05 to 0.4 µg/ml), and silver (0.2 to 1.5 µg/ml) were prepared from salts of chemically pure and ultrapure metal salts. An air and acetylene flame was used, and all measurements were made on a Tekhtron AA-4 atomic absorption spectrophotometer (manufactured by Varian). The rate at which the vapor source dissolved from the aerosol drops, the evaporation of solid particles, and the dissociation of the compounds all affected the distribution of atoms along the flame's height. The maximum concentration of Zn, Pb, and Ag atoms were found to be located at heights of 10.00, 8.00, and 7.00 mm over the burner base, respectively. The sensitivity and precision of the atomic absorption determination was also affected by the make-up of the gases of the air and acetylene flame; comparisons of the sensitivity and precision of determinations in stoichiometric, reducing, and oxidizing flames (i.e., in flames with respective combustible:oxidizing agent (C:O) ratios of 1.00, 1.26, and 0.8) revealed that a stoichiometric flame is best in that it is far more sensitive than is an oxidizing flame and more stable and nearly as sensitive as a reducing flame is. Determining below-minimum allowable level quantities of the three impurity elements studied required that they be subjected to preliminary concentration. A procedure combining sorption concentration of the elements on SG-80 modified by 2-aminothiazole prior to atomic absorption determination was recommended as effective for use in monitoring the content of Pb and Ag in drinking water lines. Figure 1, tables 2; references 3 (Russian).

UDC 547.241+632.95

Synthesis and Pesticide Activity of N- and C-Phosphorus-Substituted Azomethine Derivatives

917M0027E Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA in Russian Vol 31 No 5, Sep-Oct 90 (manuscript received 14 Apr 89) pp 515-520

[Article by M.M. Kabachnik, I.A. Chadnaya, Ye.V. Snyatkova, Z.S. Novikova, G.L. Abramova, N.G. Rozhkova, and Ye.I. Andreyeva, Organic Chemistry Department, Moscow University]

[Abstract] N- and C-phosphorus-substituted azomethines have been recently comparatively little studied as opposed to other organophosphorus compounds. Most of the work that has been done with regard to them deals with the synthesis and selected properties of phosphorus (V)-substituted aldamines; azomethines, which contain a tricoordinated phosphorus atom in their molecule, have been studied far less. The authors of this article have, for a number of years, conducted systematic research regarding the synthesis and reactivity of N- and C-phosphorus-substituted azomethines and have searched

for new such compounds that would proved useful. In the study reported herein, they synthesized 10 phosphonium salts of C-phosphorus (III)-substituted azomethines, examined their pesticide activity, and compared their activity with that of nonsubstituted azomethines. The compounds were synthesized in accordance with procedures that are described in detail. Next, their pesticide activity was evaluated at the All-Union Scientific Research Institute of Chemical Plant Protectants. The studies showed that all phosphorylated compounds, regardless of whether the phosphorus atom was located at the nitrogen atom or at the carbon atom, manifest high pesticide activity when compared with nonphosphorylated azomethines. Two of the 10 compounds synthesized possess high growth-regulating properties, two of the N-phosphorylated compounds enamined manifest a medium degree of fungicidal activity, and four C-phosphorus (III)-substituted azomethines have proved to be active as herbicides and insectoacaricides. Only one of the compounds synthesized manifested an in vitro fungicidal effect; however, most manifested a medium degree of fungicidal activity in vivo. Tables 2; references 12: 11 Russian, 1 Western.

UDC 662.73-541.6:547.9

**Chemical-Structural Features of Brown Coals
From the Kansk-Achinsk Basin**

917M0023A Moscow KHIMIYA TVERDOGO
TOPLIVA in Russian No 5, Sep-Oct 90 (manuscript
received 14 Dec 90) pp 3-8

[Article by Ye.B. Lesnikova, Ye.A. Grigoryeva, S.G. Gagarin, V.P. Lukicheva, O.A. Dementyeva, and L.V. Shulyakovskaya, Mineral Fuels Institute]

[Abstract] The large reserves of low-sulfur and low-ash coals of the Kansk-Achinsk Basin are a promising raw material base for refining; however, using brown coals as a commercial raw material requires in-depth knowledge of the make-up, chemical-structural features, and nature of the organic bonds affecting the coal's reactivity. The literature contains very little in the way of data on the relationship between the structure and reactivity of brown coals during the process of their breakdown. The authors of the study reported herein used modified methods of directed chemical destruction, i.e., hydrolysis, reduction, and transalkylation, to gain more information about the brown coal of the Kansk-Achinsk Basin. They found ester bonds accounting for 25 to 60% of the "unaccounted-for" forms of oxygen and alkyl bridge bonds combining the aromatic fragments of the coal's structure in a quantity ranging from 1.7 to 4.8 $\text{CH}_2/100 \text{ at.C}$ ($r = 0.64$). They also discovered a correlation between the presence of ester bonds in the coal's make-up and its activity with respect to reduction. Mathematical and statistical processing of the resultant data enabled the authors to derive coefficients of the pair correlation between the petrographic and chemical characteristics of the coals studied. Because the different coal samples taken from the basin were found to possess a broad set of structural and chemical characteristics that could cause significant differences in their reactivity, they plan to devote more research to studying the traits distinguishing samples from the basin's different beds. Figure 1, tables 4; references 16: 10 Russian, 6 Western.

UDC 536.7

**Coal Formation When Methane Comes Into
Contact With an Inhomogeneous Mixture of the
Commercial Catalyst GIAP-8 and Zirconium
Dioxide**

917M0023B Moscow KHIMIYA TVERDOGO
TOPLIVA in Russian No 5, Sep-Oct 90 (manuscript
received 28 Jul 89) pp 14-17

[Article by V.G. Lipovich, A.T. Pyatenko, M.Yu. Nizhegorodova, and Ye.Yu. Elimelakh, High Temperatures Institute, USSR Academy of Sciences]

[Abstract] Catalytic conversion of natural gas is currently the main source of hydrogen in industry. Nickel-containing heterogeneous catalysts are the most effective

catalysts for the gas conversion process; however, because they are subject to a high degree of carbonization, using such catalysts not only reduces the capacity of the catalytic units used but also results in a sharp worsening of the catalytic reactor's dynamic characteristics. The authors of the study reported herein used the thermogravimetric analysis method to examine the carbon formation that occurs when methane comes into contact with a mechanical mixture of heterogeneous contacts. In their studies, nickel is replaced by the commercial nickel-containing catalyst GIAP-8, which is used commercially for the steam conversion of refinery gases and which is actually a mixture of Ni and Al oxides applied to the surface of a granulated carrier made of large-pore corundum. They also included zirconium dioxide in their catalyst mixture and studied its effect on the rate of carbide deposit formation and on the activation energy and specific coke clogging of GIAP-8 when it comes into contact with methane. Each experiment consisted of two stages, namely, reduction (catalyst activation) and coke clogging. The starting specimens were first subjected to reduction by heating in a hydrogen stream at a rate of $20^\circ\text{C}/\text{min}$ until a temperature of 450°C was reached. They were then cooled to room temperature in an argon atmosphere and subjected to carbonization in a methane and argon stream ($\text{CH}_4:\text{Ar} = 2:1$). It was discovered that, unlike the coke clogging of pure metallic nickel, the process of coke clogging of the nickel mixture used occurs in two stages. Adding different quantities of zirconium dioxide did not change the qualitative picture of the process. It did, however, reduce the specific coke clogging of the GIAP-8 in a heterogeneous mixture. Although this qualitative effect was small, the very fact that the specific coke clogging was reduced confirms that the effect of zirconium dioxide in a mechanical mixture cannot be reduced to simple dilution. As the GIAP-8 was diluted with zirconium dioxide from 0 to 80%, the maximum rate of coke clogging in the low-temperature range decreased by an order of magnitude. In the high-temperature range, on the other hand, it was reduced by about a factor of 3. Calculations of the kinetic parameters of the carbonization process confirmed that adding zirconium dioxide largely affects the mechanism of carbon formation in the low-temperature range. Figures 4; references 4 (Russian).

UDC 543:544

**Studying Oil Asphaltenes by the Reverse Gas
Chromatography Method**

917M0023C Moscow KHIMIYA TVERDOGO
TOPLIVA in Russian No 5, Sep-Oct 90 (manuscript
received 28 Jul 88) pp 22-24

[Article by E.R. Nabiullina and F.Kh. Kudasheva, Bashkir State University]

[Abstract] The reverse gas chromatography method is superior to other methods used to study oil residues in that it is simple, quick, and economical and yields

reproducible results. The authors of the study reported herein used the method of reverse gas chromatography to study asphaltenes and carbones of petroleum pitch. The asphaltenes were isolated in accordance to the generally accepted method based on the Gold "hot" method and fractionated in accordance with a procedure described elsewhere. The chloroform-soluble portion was removed from the carbones selected for study. The resultant fractions were applied onto dynachrome-H as a stationary liquid phase in a quantity equal to 20% of the mass of the solid carrier. The studies were conducted on an LKhM-8MD gas chromatograph on a 1 x 0.03-m column at a nitrogen carrier-gas rate of 40 to 60 ml/min. The columns were stabilized for 8 hours at temperatures of 40 to 80 °C. The retention of the standard compounds was determined in the temperature range from 80 to 230 °C, with different classes of compounds (i.e., alcohols, ketones, paraffin-series hydrocarbons, aromatic hydrocarbons, and thiophene) serving as the standards. Because the retention of sorbates depends on the amount of specimen added, the true retention times were determined by extrapolation to a zero specimen. The dependence of the log of the specific retained volume on the inverse temperature was determined for the test specimens; this dependence is complex and has several breaks, which is inherent to polymers with a mesomorphic structure. The specimens taken were characterized by high aromaticity factor values as obtained by PMR spectrometry (0.66 to 0.78) and significant percentages of condensed carbon atoms (from 24.6 to 52.50%). An inversion of the benzene and thiophene chromatographic peaks was observed; this confirmed the presence in the specimens of organized aromatic lattices similar to those of graphite crystallite. A reaction between the sorbates and sorbent molecules that increased in proportion to the dipolar moments and boiling points was characteristic of the petroleum pitch asphaltenes. In the case of thiophene, the sulfur heteroatom was observed to shift the plane of the molecule away from the contact face of the adsorbent's hydrocarbon structure, which explains the lower sorption heat values found in the case of thiophene than in the case of benzene. The high values of the coefficients of the reaction of the heteroatomic sorbates that were found indicate that polar compounds are included in the make-up of the asphaltenes and carbones studied, hence the conclusion that the asphaltenes and carbones of the petroleum pitch of pyrolysis resin are highly aromatic condensed structures with properties of mesomorphic polymers. Figure 1, tables 2; references 7: 4 Russian, 3 Western.

UDC 665.7.032.56:529.16

Using Radioactive Tetralin To Study the Coal Liquefaction Process

917M0023D Moscow *KHIMIYA TVERDOGO TOPЛИVA in Russian* No 5, Sep-Oct 90 (manuscript received 28 Jun 88) pp 32-37

[Article by M.F. Polubentseva, V.V. Duganova, G.A. Mikhaylenko, I.E. Pikerskiy, N.V. Chernetskaya, and

V.G. Lipovich, Institute of Petrochemical and Coal Chemical Synthesis, Irkutsk University]

[Abstract] Tetrahydronaphthalene [Tetralin] is widely used in refining coal into synthetic liquid fuel and raw material for the chemical industry. The authors of the study reported herein examined the process of the low-temperature processing of coal in a solvent medium in the presence of the following catalysts: anhydrous chloride and iron (III) sulfate and their crystalline hydrates. The research object was brown coal from the Irsha-Borodino deposit in the Kansk-Achinsk Basin. It had the following characteristics (%): W^a , 1.3; A^{daf} , 5.4; V^{daf} , 47.8; C^{daf} , 72.1; H^{daf} , 5.2; N^{daf} , 0.8; and $(S + O)^{daf}$, 21.9. The coal:solvent:catalyst ratio was kept equal to 1:10:1 in all of the experiments. The liquefaction was conducted in a microautoclave with a volume of 40 cm³ at a temperature of 350 °C for 30 minutes in the absence of molecular hydrogen. At the end of the experiment, the reaction products were rinsed with water to break down the catalyst and extracted by hexane, benzene, and pyridine to liberate the oil, asphaltenes, and preasphaltenes, respectively. The make-up of the regenerated solvent was determined on a Khrom-4 chromatograph. It was discovered that iron (III) sulfate exhibits high catalytic activity during the process of the liquefaction of coal in the presence of a hydrogen donor solvent and that crystalline hydrates of iron (III) salts help increase the yield of preasphaltenes. The radiometric analysis conducted demonstrated that Tetralin reacts with the products of the decomposition of the coal matter with varying intensities. These intensities depend on the nature of the catalyst. Tables 5; references 11: 1 Russian, 10 Western.

UDC 662.475:522.7

Effect of the Make-Up of Mineral Impurities on the Rheological Properties of Water and Coal Suspensions

917M0023E Moscow *KHIMIYA TVERDOGO TOPЛИVA in Russian* No 5, Sep-Oct 90 (manuscript received 13 Sep 89) pp 76-81

[Article by V.G. Samoylik, A.T. Yelishevich, and A.S. Makarov, Donetsk Polytechnic Institute, UkSSR Ministry of Education]

[Abstract] The effectiveness of highly concentrated water and coal suspensions, which constitutes a new type of liquid fuel, is largely determined by their rheological parameters during the process of their transportation and storage. Highly concentrated water and coal suspensions with the required rheological characteristics are produced by keeping the concentration of special chemical additives and solid phase at the specified level and by keeping the granulometric and mineral make-up of the latter constant. The most efficient way of accomplishing this is to use a suspension of coal from one mine seam (whose organic and mineral mass exhibits virtually constant properties) as the solid phase. Stabilizing the

parameters of highly concentrated water and coal suspensions becomes more complicated when the raw material base of the hydraulic transport systems includes coals from different shafts and reserves, which sometimes differ significantly from one another not only from the standpoint of content but also from the standpoint of accompanying rock. The study reported herein examined the effect of different mineral impurities on the rheological properties of highly concentrated water and coal suspensions and determined the range of permissible contents of these impurities in the solid phase of a water and coal suspension. Kuzbass coals were used as the research object. Petrographic analysis was used to determine the principal components of the inorganic components of the solid phase of water and coal suspensions of the test coals. It was established that montmorillonite (which facilitates the formation of a three-dimensional coagulation structure with a minimal amount of solids and causes the abrupt hardening of this structure upon a transition to more concentrated suspensions) exerts the greatest effect of structure formation in water and coal suspensions. The effect of hydromica, while analogous, is less pronounced. Kaolinite reduces the strength of the coagulation structure of water and coal suspensions; however, its stabilizing effect is lower than that of other agrillaceous minerals. The presence of quartz in the solid phase causes the suspension to stratify. Obtaining highly concentrated water and coal suspensions with good rheological characteristics requires reducing the content of mineral impurities in the solid phase to a specified level that depends on the make-up of the impurities in question. Figures 4, tables 2; references 6 (Russian).

UDC 620.193.4:622.693.4

Ways of Reducing Corrosion During the Pipeline Transport of Water-Coal Pulps

917M0023F Moscow KHIMIYA TVERDOGO
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received 21 Dec 89) pp 82-85

[Article by A.L. Antonova, V.L. Basenkova, and A.V. Butyugin, Donetsk State University]

[Abstract] The problems of the corrosion wear of pipe steels used in transporting water and coal pulps and ways of protecting steel against corrosion are becoming critical in view of the development of pipeline hydraulic transport of solid fuels that is being planned in the USSR. The authors of the study reported herein examined the effect of the pH level of water and coal pulp and various inhibitors on the corrosion wear of pipe steel. In view of past research demonstrating that the NaOH, $\text{Ca}(\text{OH})_2$, and sodium silicate generally used to inhibit the corrosion process are subject to a rapid loss of their corrosion-inhibiting properties because of the high absorbency of grade D coal (Kuzbass coal) that in turn lowers the inhibitors' pH levels, the authors proceeded in the direction of developing inexpensive and readily

available composite additives that would be able to maintain high pH levels for a rather long period of time, i.e., that would possess elevated buffer properties relative to OH ions. As potential inhibitors possessing the required properties, the authors tested humates, a mixture of $\text{Ca}(\text{OH})_2$ and sodium humates, and a mixture of CaO and humates. It was discovered that a combination of $\text{Ca}(\text{OH})_2$ and sodium humates is much more effective in inhibiting the corrosion of steel pipelines used to transport water and coal pulps than is using humates or calcium hydroxide alone. The following was recommended as being the optimum composition: $\text{Ca}(\text{OH})_2$ in a quantity from 0.2 to 0.6 mass percent and humates in a quantity from 0.05 to 0.5 mass percent. Because of the delay in the bonding of the CA^{+2} ions by the coal, there is no need for repeated addition of hydroxide to the pulp as it is expended during transportation, which reduces the corrosion-erosion wear of pipeline steel. Tables 4; references 14: 12 Russian, 2 Western.

UDC 662.74:66.097.3

Catalytic Hydrogasification of Coals From the Kansk-Achinsk Basin on Hydrides of Intermetallides

917M0023G Moscow KHIMIYA TVERDOGO
TOPLIVA in Russian No 5, Sep-Oct 90 (manuscript
received 7 Dec 88) pp 92-95

[Article by I.D. Chagayeva, S.N. Khadzhiev, Kh.N. Askhabova, and V.V. Lunin, Grozno Petroleum Scientific Research Institute]

[Abstract] The hydrogasification of carbon-containing materials for the purpose of producing synthetic natural gas is currently receiving a great deal of attention. Whether a technology to implement this process will be created will largely be determined by the outcome of the search for effective catalysts capable of being easily separated from the residues of unreacted coal and ash and then regenerated. The authors of the study reported herein examined the gasification of coals in the presence of catalysts based on the intermetallide hydrides $\text{ZrNiH}_{2.8}$, $\text{ZrCoH}_{2.8}$, $\text{ZrFeH}_{2.8}$, $\text{HfNiH}_{2.8}$, $\text{HfCoH}_{2.8}$, and ZrNiMoH . Coals from the Berezovka and Irsha-Borodino deposits of the Kansk-Achinsk Basin and low-temperature coke from the Irsha-Borodino deposits were used as the raw materials. The hydrogasification of the materials was conducted in a flow-through device at atmospheric pressure in the temperature range from 300 to 1,000°C in a hydrogen stream. It was discovered that both the catalytic properties of the hydrides and the nature of the carbon material used affect the make-up of the products and their degree of conversion. The total conversion of coal in the presence of intermetallide hydride-based catalysts remained at the level of a non-catalytic process; however, the make-up of the reaction products changed sharply. Methane was the main reaction process in the catalytic process. In the noncatalytic process, on the other hand, the hydrocarbons $\text{C}_2\text{-C}_4$, CO,

and CO_2 were detected in the gas along with CH_4 , and their intense resin formation was also observed. Of the test catalysts, $\text{ZrNiH}_{2.8}$ showed the greatest activity; in its presence the methane yield increased by an order of magnitude when compared with the noncatalytic process. The conversion of the Irsha-Borodino coal amounted to 40.8 mass percent, and that of Berezovka coal amounted to 36.7 mass percent. The coals studied were close from an elemental make-up standpoint; however, the Irsha-Borodino coal (content of volatile matter, 36.7 mass percent) was subject to greater gasification damage than was the Berezovka coal (which contained 41.22 mass percent volatile matter). The conversion of low-temperature coke was much lower (19.9 mass percent), while its content of volatile matter amounted to 21 mass percent. The methane yield also increased in proportion to the content of volatile matter. It was concluded that the deactivation of catalysts based on intermetallide hydrides during the hydrogasification process is likely connected with the agglomeration of nickel particles and the formation of nickel sulfide on the catalyst's surface. Figures 3, tables 2; references 16: 12 Russian, 4 Western.

UDC 662.74

Change in the Paramagnetic Properties of Coals From the Kansk-Achinsk Basin During the Hydrogasification Process

917M0023H Moscow KHIMIYA TVERDOGO
TOPLIVA in Russian No 5, Sep-Oct 90 (manuscript
received 7 Mar 89) pp 96-99

[Article by I.D. Chagayeva, S.N. Khadzhiev, Kh.N. Askhabova, and Ye.V. Lunina, Grozno Petroleum Scientific Research Institute]

[Abstract] The authors of the study reported herein examined the paramagnetic properties of coals from the Kansk-Achinsk Basin and the solid residues of their hydrogasification. Irsha-Borodino and Berezovka coals and low-temperature coke of Irsha-Borodino coal served as the test objects. Solid residues were obtained during the process of the coals' gasification at 400-600°C. Electron paramagnetic resonance [EPR] spectra were recorded on a type RE-1306 radio spectrometer at a frequency of 9,300 MHz. The concentration of paramagnetic centers was determined by comparing the integral intensities of the EPR spectra of the test and standard specimens by using an intermediate standard (Cr^{3+} in corundum). The relative error did not exceed 15%. The line width was determined by extrapolation to zero values of the high-frequency modulation amplitude. The spectra were recorded in air and in a vacuum of 10^{-2} torr. The concentration of paramagnetic centers in the initial coals was an order of magnitude lower than in the low-temperature coke. As the temperature of the process and the degree of coal and low-temperature coke conversion increased, the concentration of paramagnetic centers increased; it reached a maximum at 400 and 500°C,

respectively. The EPR spectra of the coals and low-temperature coke in air were in the form of a singlet line, whereas those of the specimens in the vacuum were in the form of the superimposition of narrow and wide lines. According to the literature, the narrow EPR lines correspond to nonvaporized electrons with a high degree of delocalization with respect to the system of conjugated bonds, whereas the wide lines correspond to free-radical fragments with a lesser degree of delocalization of the nonvaporized electron. The oxygen air was found to have a significant effect on the parameters of the EPR spectra, with the EPR spectra recorded in air being much less intense than those recorded in a vacuum. The width of the spectrum was found to depend on the distance between the paramagnetic centers and the oxygen molecule. At a distance of more than 60 angstroms, the oxygen had virtually no effect on line width. The increase in the concentration of paramagnetic centers (by an order of magnitude) under process conditions accompanied by a reduction of the H/C ratio in solid residues indicates significant destruction of the coals with breaking of the C-C bonds. The change in paramagnetic properties observed is in good agreement with existing ideas regarding the structure of coals. Figures 2, table 1; references 6 (Russian).

UDC 504.06:621.182.94:541.183

Sorption of Heavy Metals by the Fly Ash From Burning Coal at TES

917M0023I Moscow KHIMIYA TVERDOGO
TOPLIVA in Russian No 5, Sep-Oct 90 (manuscript
received 9 Jun 89) pp 100-103

[Article by I.Z. Pertsikov and Ye.P. Suslova, Irkutsk Polytechnic Institute]

[Abstract] Interest has recently been expressed in using the ash residues from the burning of solid fuels as sorbents of organic and inorganic matter. Ash is already being used to clean cyanides, petroleum products, phosphates, and organic matter from waste waters. The authors of the study reported herein conducted a systematic study of the sorption of a number of heavy metals (Cu, Zn, Ni, Pb, and Cr) in the fly ash from the burning of azeyskiy [transliteration] coal. Two types of fly ash were taken from two sections of an electrostatic precipitator that was part of the dry fly-ash collection system at a thermal power plant [TES]. Each had different contents of SiO_2 , Fe_2O_3 , Al_2O_3 , CaO , and MgO . For the sorption of Cu, Zn, Pb, Ni, and Cr, the authors used an aqueous solution with the following concentrations of elements ($\mu\text{g/ml}$): Cu, Cr, and Pb = 3.0, and Zn = 30.0. The studies of the ashes' absorbency were conducted at a solution temperature of 20°C with continuous mixing. A quantity of 100 ml of solution was used; in other words, the starting solution contained 300 μg Cr, Cu, and Pb and 3,000 μg Zn. It was discovered that the ashes studied are good sorbents with respect to Cu, Cr, and Pb. Thus, even in a solid:liquid ration of 1:100 for 10 minutes of

contact, the residual concentration of these metals in the solution was insignificant and far below the maximum allowable concentration, whereas the degree of sorption of the first ash solution tested was above 99%. Absorbency with respect to Zn and Ni was much lower and only reached rather high values in the case of high values of the solid:liquid ratio. The ashes' sorption of Ni and Zn was found to be influenced by the pH of the solution. No significant differences between the absorbencies of the two solutions tested were observed. Both ash solutions tested were recommended for use in cleaning these elements from waste waters. Figures 2, table 1; references 3 (Russian).

UDC 669.2/8.061.34:621.311.22

The Hydrolytic Stability of Heavy Metal Compounds in Fly Ash From TES

917M0023J Moscow KHIMIYA TVERDOGO
TOPLIVA in Russian No 5, Sep-Oct 90 (manuscript
received 26 Oct 89) pp 104-106

[Article by Ye.P. Suslova and I.Z. Pertsikov, Irkutsk Polytechnic Institute]

[Abstract] The prospects of the development of power generation presuppose the more complete use of coals in the mass consumption of fuel. The authors of the study reported herein examined the process of the leachability of heavy metals from the dry ash from thermal power plants [TES] under static conditions in aqueous media with different pH levels. They studied averaged ash sampled from one to four sections of an electrostatic precipitator. The test specimen had the following make-up (%): SiO_2 , 59.8; Al_2O_3 , 24.9; Fe_2O_3 , 7.1; CaO , 4.1; MgO , 1.3; and other compounds, 2.8. After undergoing attrition, the test specimen was subjected to leaching in a neutral medium (pH 6-7) at a temperature of 20°C for 30 minutes, leaching in an acid medium (pH 2-3) at a temperature of 20°C for 30 minutes, and leaching in an alkaline medium (pH 12) for 30 minutes at 20°C. The leaching out of the heavy metals was most intense in the acid medium. Ni, Cu, and Mn only passed from the ash and into the metal in the acid medium; virtually no formation of soluble forms of the metals occurred in the alkaline medium. Metals such as Zn and Pb were leached out in both acid and alkaline media (albeit to a somewhat lesser degree in the latter). The overall degree of transfer of heavy metals to solutions with the different pH levels examined was rather low; however, the data obtained indicated that it is indeed possible to use high-calcium ashes to deacidify soil. When such ashes are added to soil, the formation of heavy metal ions will be low; however, the level of their formation must be investigated in each specific instance. Figure 1, table 1; references 5: 3 Russian, 2 Western.

UDC 666.613

Forecasting the Direction in Which Ashes of Solid Fuels Are Used in Construction

917M0023K Moscow KHIMIYA TVERDOGO
TOPLIVA in Russian No 5, Sep-Oct 90 (manuscript
received 6 Jan 89) pp 107-111

[Article by M.A. Savinkina, A.T. Logvinenko, V.N. Zyryanova, and N.Z. Lyakhov, Institute of the Chemistry of Solid Fuel and Mineral Ore Refining, Siberian Department, USSR Academy of Sciences]

[Abstract] The ashes of solid fuels are rather diverse with respect to their chemical make-up; they consist primarily of SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , SO_3 , and R_2O ; however, the ratio of the oxides fluctuates within broad limits, changing the ashes from acidic to highly basic. After analyzing the literature and data from their own experiments, the authors of the study reported herein concluded that the technological properties of ashes depend primarily on their content of CaO and losses during calcination. The latter are characterized by the presence of carbon loss and insignificant amounts of moisture and CaCO_3 in the ashes. During the course of their studies, the authors examined the make-up of fly ash specimens from the electrostatic precipitators at TES. Fly ash specimens resulting from the burning of five types of fuel were studied: Kuznetsk coal, Tyumen peat, and coals from three beds in the Kansk-Achinsk Basin. After analyzing their results, the authors developed specific recommendations regarding the applications of each of these five classes of fly ash in construction. The ashes belonging to the first class were found to have a plasticizing effect, and those in the second class were recommended as additives (i.e., hydrolytically active additives with a plasticizing effect) for cement, lime, and gypsum. The high-calcium ashes belonging to the third class were recommended as additives to cement used in rural, road, and low-story construction, whereas the ultra-high-calcium ashes in the fourth class were recommended for use in producing autoclave products or mixed binders with special additives. The class 5 ashes were recommended for use as lightweight porous filler. The ashes of all five classes were recommended for use as a raw material for use in clay brick and cement. Figures 2, table 1; references 5 (Russian).

UDC 541.183.661.662.73

The Pore Structure and Chemical Nature of the Surface of Carbon Sorbents Based on Coal in Different Stages of Metamorphism

917M0023L Moscow KHIMIYA TVERDOGO
TOPLIVA in Russian No 5, Sep-Oct 90 (manuscript
received 29 Mar 89) pp 111-114

[Article by S.S. Stavitskaya, A.A. Larina, I.A. Tarkovskaya, and O.V. Zakolodyazhnaya, Physical Chemistry Institute, UkSSR Academy of Sciences]

[Abstract] Mined coals are one of the main raw material sources of activated charcoals, which have long been renowned as sorbents of gases, vapors, and dissolved matter and which have traditionally been used to isolate, separate, and clean various substances in the chemical, food, and other sectors of industry, not to mention in water protection and water treatment. The authors of the study reported herein used various chemical, physico-chemical, and physical methods to compare the pore structure and chemical nature of the surface of coals and activated charcoals based on them. They obtained detailed information on the structural-sorption and ion exchange characteristics of coals in different stages of metamorphism and activated sorbents based on them: UP-1, UP-2, and UP-T; AU-2, AU-6, AU-9, AU-10, and AU-13, all of which exhibit good uptake of CuSO_4 ; and AU-1, AU-11, AU-12, AU-14, AU-15, and AU-16, all of which exhibit poor uptake of CuSO_4 . The pore structure and chemical make-up of the test specimens were examined in the various stages of their processing: granulation, drying at room temperature, carbonization at 874 K, and activation in a stream of steam at different temperatures from 1,123 K to 1,223 K. It is demonstrated that sorbents possessing a primarily microporous structure (regardless of the grade of coal from which they are produced) are best for use in manufacturing effective chemical absorbents and drying agents because they are best able to absorb modifying additives such as copper sulfate. The stage of the starting coals' metamorphism did not appear to influence the performance of the resultant absorbents. Figures 3, tables 2; references 12 (Russian).

UDC 661.666.2

Selected Research on Properties of Fibrous Materials

917M0023M Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 5, Sep-Oct 90 (manuscript received 5 Dec 88) pp 123-126

[Article by A.M. Kolosova, M.I. Rogaylin, and N.N. Kovalevskiy, deceased, Mineral Ores Institute]

[Abstract] Engineering progress in the field of aircraft and rocket construction, space technology, and a number of other related fields is closely tied to progress in creating new fibrous materials combining high mechanical indicators and heat resistance. Research in this field is currently being conducted in two directions: improving the process of producing carbon materials and studying their structures and properties. The authors of the study reported herein examined the properties of heating elements during the process of their formation by the method of packing fibrous carbon materials with pyrocarbon. During the course of their research, they studied the kinetics of the process of saturation of the pore space of ShTU-3 carbon cord woven from the fiber Ural-24. The research was conducted in a small pyrolysis furnace at a process temperature of 1,050°C. The change

in the make-up of the composite carbon-carbon material during the process of its formation was determined, and the dependence of the composite's make-up on pyrolysis time was plotted. The test cord was also subjected to thermogravimetric analysis. It was discovered that the cord remains stable up to a temperature of 525°C, after which it loses mass during the heating process. By a temperature of 1,000°C the initial ShTU-3 cord burns completely without leaving any residue, whereas pyrocarbon-impregnated cord does not begin to decompose until it reaches a temperature of 600 or 700°C (in the cases of ShTU-3-PU-1 and ShTU-3-PU-2 cord, respectively), with 43 and 65% solid residues remaining at 1,000°C, respectively. Mercury porosimetry studies of fibrous composite based on ShTU-3 revealed that the degree of packing may be regulated by varying the temperature regimen of the process. Figures 6, tables 2; references 3 (Russian).

UDC 537.322+661.66

Anisotropy of the Thermoelectromotive Force of Carbon Materials

917M0023N Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 5, Sep-Oct 90 (manuscript received 28 Mar 90) pp 137-138

[Article by A.S. Kotosonov, I.Ya. Levintovich, V.I. Volga, and Ye.V. Logacheva]

[Abstract] Previous research has demonstrated that the thermoelectromotive force of weakly textured polycrystalline graphites should coincide (with respect to magnitude) with the thermoelectromotive force of crystallites, i.e., α_1 , along the base axis of the plane and does not depend on the measurement direction. The magnitude of α_1 is determined by the concentration, mobility, and sign of the charge carriers and is a parameter that is sensitive to defects in the graphitelike layers. Anisotropy of thermoelectromotive force should appear solely in materials with a clearly expressed plane-type texture such as pyrographites and quasi-monocrystals of graphite. This concept contradicts the results of earlier studies noting differences in the thermoelectromotive forces of specimens cut from blanks of polycrystalline graphite in different directions relative to the pressing axes. Experimental confirmation of the theoretical assessments that have been made is fundamental to interpreting the magnitude of the thermoelectromotive force of carbon fiber, which is measured when thermoelectric contacts are connected to the side surface of the fiber. The thermoelectromotive force thus measured should coincide with that of the crystallites, α_1 , regardless of the fiber's texture. The anisotropy of the thermoelectromotive force of carbon fibers may also be indirectly estimated on the basis of the anisotropy of the thermoelectromotive force of composites consisting of it. The authors of the study reported herein experimentally determined the anisotropy of the thermoelectromotive force of a number of materials with a pronounced

texture. They prepared model specimens from coke and sand composites and carbon-carbon composites based on carbon fibers and fabric with a significant anisotropy of their properties. Specimens 5 x 5 x 40 mm in size were cut along the various directions of the minimum and maximum anisotropy of the specific electric conduction. In recrystallized graphite these directions coincided respectively with the direction of the pressing axis and the direction perpendicular to it, in uniaxially reinforced and plane-reinforced composites they coincided with the reinforcement axis (plane) and the direction perpendicular to it, and in biaxially reinforced composite these direction coincided with one of the reinforcement axes and the bisectrix of the angle between them. The resultant data enabled the authors to conclude that when measuring the thermoelectromotive force of carbon materials, the effect of specimens' textures may be ignored when arranging the thermoelectric sensors on them. Table 1, references 3: 1 Russian, 2 Western.

UDC 661.6

Disproportionation of Carbon Monoxide on Iron Oxide Catalysts

917M00230 Moscow *KHIMIYA TVERDOGO TOPLIVA* in Russian No 5, Sep-Oct 90 (manuscript received 19 Jul 89) pp 139-142

[Article by N.S. Pechuro, V.K. Frantsuzov, Ye.A. Sinelnikova, B.V. Peshnev, and O.Yu. Komarova, Moscow Institute of Fine Chemical Technology]

[Abstract] Disproportionation of carbon monoxide, resulting in the formation of carbide deposits, is one of the side reactions in syntheses based on CO and H₂. This reaction is of interest to researchers because the surface carbon participates in the formation of hydrocarbons

and oxygen-containing compounds and helps change the chemical and crystallographic make-up of catalysts. The fibrous carbon formed during the disproportionation of CO is, moreover, interesting in its own right since it possesses a set of valuable properties that are characteristic of composites. The authors of the study reported herein researched the disproportionation of CO on iron oxide contacts to discover the nature of its catalytically active phases and the main laws governing the reaction. As catalysts they used Fe₂O₃ and Fe₂O₃ with MgO additives. They produced the contacts by precipitating the respective hydroxides from salt solutions and subsequently forming and drying the paste to a constant mass at 110°C. This was followed by calcination for 5 hours at 500°C. The studies were conducted in a flow-through quartz reactor in the temperature range from 450 to 650°C and with volumetric CO feed rates of 1,000 to 2,700 h⁻¹. Carbon monoxide was obtained by breaking down formic acid with sulfur at 60-80°C and subsequently cleansing it of gaseous impurities and steam. The make-up and amount of resultant gas were determined. X-ray phase analysis was used to estimate the solid-phase transformations; the analysis was conducted on a DRON-2. It was discovered that intensive development of disproportionation was preceded by the occurrence of a reduction of the contact, which was indicated by the significant quantity of CO₂ in the gas in the initial period. This led the authors to hypothesize that, simultaneously with the reduction of the contact, active centers form that are responsible for the disproportionation of carbon monoxide and thus result in the formation of fibrous carbon. Adding MgO to the contact resulted in the formation of lower iron oxides and increased the activation energy of the reaction of the disproportionation of carbon monoxide. It was thus concluded that the formation of fibrous carbon occurs in carbide phases and may be expressed in terms of a kinetic equation allowing for the strong adsorption of the reaction products. Figures 3, tables 3; references 11 (Russian).

UDC 541.6.68:538.569

Structure and Properties of Network Copolymers Containing Urethane Fragments, Cyanurate, and Isocyanurate Cycles

917M0020C Kiev UKRAINSKIY KHIMICHESKIY
ZHURNAL in Russian Vol 56 No 9, Sep 90
(manuscript received 18 Sep 89) pp 576-579

[Article by G.M. Semenov, S.Yu. Lipatov, A.M. Faynleyb, T.A. Shantaliy, and L.M. Sergeyeva, Institute of High-Molecular Compounds Chemistry, UkSSR Academy of Sciences, Kiev]

[Abstract] The goal of this work was to investigate the structure of copolymers obtained by concurrent polycyclotrimerization of macrodiisocyanate (MDC) with a relative molecular weight of 1,000 and 2,4-toluylenediisocyanate with the dicyanate ester of 2,2'-diphenylolpropane (DPP). The DPP content was varied from 0.1 to 2 mol/mol MDC. The reaction was catalyzed by a triethylamine-diglycidyl ester complex at a molar ratio of 1:5. The copolymers obtained were investigated by IR internal reflection spectroscopy as well as by dielectric relaxation. It was shown that the structure of cross-linking nodes and the network of physical bonds can be affected by varying the ratio of the starting materials used in the above synthesis. Consequently, this could lead to altered relaxation characteristics of the synthesized copolymers. Figures 4; references: 5 (Russian).

UDC 541.64:542.954

Oligomer Anion-Active Surfactants With a Regulated Number of Terminal Groups

917M0020D Kiev UKRAINSKIY KHIMICHESKIY
ZHURNAL in Russian Vol 56 No 9, Sep 90
(manuscript received 31 Jul 89) pp 979-984

[Article by V.V. Shevchenko, Yu.S. Lipatov, A.Ye. Faynerman, N.S. Klimenko, and S.N. Loshkareva, Institute of High-Molecular Compounds Chemistry, UkSSR Academy of Sciences, Kiev]

[Abstract] Oligourethanes with terminal ionic groups exhibit surface activity at the interface between the aqueous solution and air, which exceeds the activity of traditional surfactants. An attempt was made to evaluate the effect of the structure of elastic and rigid blocks as well as the number of ionic groups at the terminals of a molecule (the structure of the anchor group) on the surfactant properties. Specifically, the study concentrated on the salts of polycarboxyl oligourethanedisemicarbazides with elastic oligoester blocks that included rigid blocks containing semicarbazide, urethane, and ester fragments along with different numbers of terminal ionic groups. It was shown that the surface activity of these compounds increased with the length of the hydrophobic components (an increase of the ionic groups from 2 to 4) and depended on the nature of the isocyanates included in the rigid blocks. An additional increase in the number of ionic groups, while keeping the remainder of the solid block unchanged, had no effect on the surface activity. Figure 1; references 9: 8 Russian, 1 Western.

UDC 678.84 + 546.287

Doping Action of Silicon-Organic Betaine on Elastomer Properties

917M0020E Kiev UKRAINSKIY KHIMICHESKIY
ZHURNAL in Russian Vol 56 No 9, Sep 90
(manuscript received 13 Jun 89) pp 990-993

[Article by Yu.R. Kolesnik, G.A. Sokolova, and I.V. Malyy, Chemical-Technological Institute, Dnepropetrovsk]

[Abstract] One of the available methods of changing polymer properties is based on doping them with chemical microadditives. The effect of an addition of 1,3-bis(1-cholinemethylidene)tetramethyldisiloxane, a highly reactive polar disiloxane betaine, on the properties of various polymers was investigated by using reverse-phase gas chromatography, IR-spectroscopy, etc. The addition of small quantities of quinolinyl betaine to the synthetic rubber SKD resulted in a marked increase in its viscosity and dielectric properties; because nothing like this was observed with the saturated materials, it was concluded that quinolinyl betaine was chemically bound to SKD. This created a system of ionic bonds in this elastomer that led to increased heat resistance and improved adhesive properties. Figure 1; references: 9 (Russian).

UDC 546.6

Phase Equilibria at 20 Degrees C in System Uranyl Fluoride-Water-Acetone

907M0310B Leningrad RADIOKHIMIYA in Russian Vol 32 No 3, May-90 (manuscript received 3 Sep 89) pp 25-32

[Abstract of article by A.A. Lychev, Va.A. Mikhalev, and D.N. Suglobov]

[Abstract] Phase equilibria in the system uranyl fluoride-water-acetone were analyzed. Anhydrous uranyl fluoride was prepared by dissolving uranium trioxide in a stoichiometric quantity of hydrofluoric acid or uranyl nitrate in excess HF, concentrating the solution at 70-80°C, then desiccating the dihydrate in a 0.1-Pa vacuum at 200°C. After determining the uranium content, the uranyl fluoride, water, and acetone were mixed in ampules that were sealed and left to stand for 3-5 days at 20±0.1°C in a crystal oven and periodically agitated. The phases were separated centrifugally, and the uranium content in the phases was measured. A weighed quantity of moist residue was analyzed for its uranium content, dissolved in a weighed quantity of water, and then analyzed for its acetone content by using PMR referenced to an internal acetonitrile standard or gas chromatography and an internal methylethylketone standard. IR spectra of the solid phases taken on an IKS-24 at 20°C revealed four regions of phase separation. Higher acetone concentrations led to reduced uranyl fluoride solubility. Region A consisted of unsaturated water-acetone solutions of uranyl fluoride. Region B (low acetone concentration), contained uranyl fluoride dihydrate with saturated water-acetone solutions. Region C (high acetone concentration) comprised water-acetone solutions of uranyl fluoride and a new phase: $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}(\text{CH}_3)_2\text{CO}$. Region D consisted of the saturated water-acetone solution and a mixture of dihydrate and dihydrate-monoacetate. The phases were found to be heterophase systems with liquid crystalline properties and were characterized by stable coagulation-dispersed structures and thixotropy. Figures 6, tables 1; references 20: 17 Russian, 3 Western.

UDC 546.841+546.799.5

The Effect of Impurities on the Size and Shape of Thorium and Americium Oxalate and Oxide Crystals

907M0310C Leningrad RADIOKHIMIYA in Russian Vol 32 No 3, May-Jun 1990 (manuscript received 10 Jul 88) pp 33-36

[Abstract of article by Ye.A. Smirnova, A.S. Kri-vokhatskiy, Yu.L. Pazukhina, and A.A. Listopadov]

[Abstract] The effect of ammonium salts and a number of surfactants on the size and shape of thorium and americium oxalate and dioxide crystals was studied.

Thorium oxalate was precipitated from solutions of thorium (0.08 and 0.8 mol/l) and nitric acid (2 mol/l) at temperatures of 20, 50, and 96°C. A 7% solution of oxalic acid (8.7 or 33.0 ml) was stirred into 10 ml of the initial solution within 5-10 seconds. The precipitates were kept in the discharge liquor at room temperature without stirring. Ammonium nitrate in concentrations of 0.06 to 2.5 mol/l served as the impurity. At 20°, the precipitate consisted of fine tetragonal platelets 1-3 µm in size, regardless of the holding time or solution composition. At 50°, a 0.8 mol/l solution with a 2.5-mol/l impurity concentration yielded, over a week's time, tetragonal platelets mostly 12-15 µm in size, with some as large as 24 µm, and about 6 µm thick. At 96°, the crystals from the 0.08-mol/l solution, with impurity concentrations of 0.25-2.5 mol/l, had the same shape and increased in size and thickness to 12-15 and 3 µ within a week's time. With the 0.8 mol/l solution, the crystal size and thickness reached 9-12 and 3-6 µm within the holding period when the impurity concentration was increased to 2.5 mol/l. The addition of the surfactants had a similar effect on the size and shape of the monodispersed crystals. The size and shape of the americium oxalate crystals were studied in a similar manner by using the isotope ^{243}Am , and a monodispersed precipitate was obtained. Thorium and americium dioxide crystals subjected to thermolysis at 850°C for 3 hours had a size and shape that matched the size and shape of the oxalate crystals, but they had linear dimensions 20-25% smaller. Figures 2, tables 2; references 3: Russian.

UDC 546.799.5:546.799.6:542.65

Separation of Americium and Curium in Persulfate-Carbonate Solutions

907M0310E Leningrad RADIOKHIMIYA in Russian Vol 32 No 3, May-Jun 90 (manuscript received 2 Jun 89) pp 121-123

[Abstract of article by A.S. Kornilov and V.M. Lebedev]

[Abstract] The behavior of americium and curium in saturated potassium sulfate solutions was studied to determine how highly pure americium could be obtained from mixtures containing different amounts of curium. A 0.4- to 0.8-mol/l solution of potassium carbonate was poured over americium and curium oxalates. Enough potassium persulfate was added so that the potassium carbonate/potassium persulfate mole fraction was between 1.12 and 2.8. The solution was held for 2 hours at 90-95°C, cooled, and allowed to stand at room temperature for 2-3 hours. With this method, 85-95% of the americium (III) oxidizes to americium (VI), which remains in solution, while the curium precipitates into a poorly soluble twin curium sulfate with potassium. Less than 0.1% Cm remains in the Am. Higher concentrations of potassium carbonate or higher potassium carbonate/potassium persulfate mole fractions have a detrimental effect on phase separation and Am purity. Tables 2; references 3: 1 Russian, 2 Western.

UDC 543.24+546.799.5+546.799.6

Quantitative Determination of Americium and Curium in Solutions by Using Potassium Phosphotungstate*907M0310F Leningrad RADIOKHIMIYA in Russian Vol 32 No 3, May- Jun 90 (manuscript received 4 Sep 89) pp 128-132*

[Abstract of article by V.M. Chistyakov, A.A. Baranov, Ye.A. Yerin, and G.A. Timoveyev]

[Abstract] Two simplified methods of titrating Am and Cm in phosphotungstate solutions were developed. The experimental solutions were prepared by evaporating an aliquotic nitric acid solution of Am beneath an IR lamp until it was dry, dissolving the solution in KRW, transferring the KRW solution to an electrolytic cell, and electrolyzing it with a PI-50 potentiostat. The oxidized solution was then displacement-titrated with thorium nitrate or redox-titrated with sodium nitrate, with the final titration point determined potentiometrically or spectrophotometrically. The change in Am and Cm ion concentrations was monitored from absorption band intensities by using SF-20 spectrophotometers and a Specord M 40. It was found that these methods can be used together to successfully determine the concentration of tri- and tetravalent americium, curium, and californium ions in KRW solutions. This is done by first dividing the KRW solution into two parts and determining the tetravalent ionic content of one of the aliquots by titration with sodium nitrate. The other aliquot is titrated with thorium nitrate to determine the total concentration of phosphotungstate ions, which are attached in the complex to the tri- and tetravalent ions. The KRW concentration is calculated under the premise that thorium (IV) and the phosphotungstate ions form a 1:1 complex. The data on the complex composition of the titrated tri- and tetravalent ions and the results of the displacement and redox titrations are used to calculate the concentration of tri- and tetravalent ions in the solution. Figures 5, tables 2; references 9; 8 Russian, 1 Western.

UDC 546.15:577.47:543.53

Using Neutron Activation to Detect Iodine 129 in Water, Soil, and Plant Samples*907M0310H Leningrad RADIOKHIMIYA in Russian Vol 32 No 3, May- Jun 90 (manuscript received 22 Jun 89) pp 150-153*

[Abstract of article by Yu.V. Kuznetsov, S.P. Rosyanov, V.K. Vinogradova, and V.M. Gavrilov]

[Abstract] A neutron activation method of detecting ^{129}I in water, soil, and plant samples is described. The water samples were prepared by adding potassium iodide and potassium carbonate to a sample, concentrating it, separating the phases, and extracting the iodine, which was

then re-extracted and a palladium iodide or lead iodate precipitated from the re-extractant. Air-dried soil samples were moistened with potassium carbonate or hydroxide and reduced to ash, which was allowed to cool and then processed with water and filtered or centrifugally separated. The sample was then concentrated, the iodine re-extracted, and the palladium iodide or lead iodate precipitated from the re-extractant. The plant samples were soaked with potassium hydroxide, dried and reduced to ash on a hot plate, processed with water, centrifugally separated, and concentrated, and palladium iodide or lead iodate was precipitated as previously described. The preparations derived from the samples were placed in quartz ampules and irradiated in an $8 \cdot 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ thermal neutron flux for 12-18 hours. Extraction was used to separate the ^{129}I from the preparations, and the dry residue was subjected to gamma-spectrometric analysis on a gamma spectrometer with a 60- cm^3 germanium-lithium detector for 20-40 minutes. The ^{129}I content was calculated from the ^{130}I lines. The ^{129}I content in the water samples varied from $60 \cdot 10^{-10}$ to $90 \text{ g/l} \cdot 10^{-10}$. The soil samples contained from 0.12 to 0.28 and the grass samples from 0.1 to 0.28 $\text{g/kg} \cdot 10^{-10} \text{ }^{129}\text{I}$. With a confidence level of 0.95, the detection error was $0.7 \cdot 10^{-9} \text{ g}$ when the average content of ^{129}I in a sample was $7 \cdot 10^{-7} \text{ g}$. Tables 1; references 14; 2 Russian, 12 Western.

UDC 666.1:621.039.73

Lead Glasses for Immobilizing Radioactive Waste*907M0310J Leningrad RADIOKHIMIYA in Russian Vol 32 No 3, May- Jun 90 pp (manuscript received 22 May 89) 162-166*

[Abstract of article by S.V. Stefanovskiy, A.A. Minayev, and F.A. Lifanov]

[Abstract] The vitrification of lead glasses for immobilizing moderately radioactive waste containing sulfates and chlorides was studied. Five different types of simulated waste designated types 1-5 were prepared from pure or analytic-grade NaNO_3 , NaCl , Na_2SO_4 , and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Real waste was also used, with one batch high in sulfates and chlorides and the other batch low in these substances. The glass was made from the real or simulated waste, PbO , pure H_3BO_3 , silica sand, and datolite concentrate in 50-g quantities in alundum crucibles in a silite-lined furnace at temperatures up to $1,200^\circ\text{C}$ with a holding time of up to 1 hour. The melts were quenched on sheet metal. Vitrification was observed visually. X-ray phases analysis was done with a Tur-M-62 diffractometer ($\text{Cu}_{\text{K}\alpha}$ radiation). The Na^+ content was determined flame photometrically, and the ^{137}Cs content was determined radiometrically on a CI-8B counter with a PS02-4 scaler. It was found that PbO-SiO_2 and $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ glasses can be used to vitrify types 1, 2 and 3 moderately radioactive wastes. The PbO-SiO_2 glasses entrap 35-40% of the types 1 and 2 and 25% of the type 3 waste oxides. The $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$

glass is particularly suited for vitrifying type 3 waste. Specimens of both types of glass containing 20 and 30% waste oxides were highly resistant to water-induced leaching. It was recommended that glasses containing 15-25% waste oxides and up to 10% sulfates and chlorides be composed of 20-40% lead, 20-40% datolite, and 20-40% silica. Glasses with higher sulfate and chloride contents should be no more than 20% waste oxides and not less than 20% lead. Figures 3, tables 3; references 10; 7 Russian, 3 Western.

UDC 621.315.592.3:548.4

Investigation of Electrophysical Properties of Irradiated Germanium-Doped With Isovalent Admixtures of Tin and Silicon

917M0018A Moscow *FIZIKA I KHIMIYA OBRABOTKI MATERIALOV* in Russian No 5, Sep-Oct 90 (manuscript received 22 Sep 89) pp 5-8

[Article by I.N. Belorukova, V.S. Garnyk, V.F. Degtyarev, Ye.V. Skudnova, and D.M. Khavdzhu, Moscow]

[Abstract] The goal of this study was to explain the effect of tin and silicon on the process of the introduction of radiation defects into the n-type germanium and on the change in its electrophysical properties. Investigation of the dose dependence of specific resistance and life expectancy of the nonessential carrier charges in the n-type germanium doped with tin, silicon, and both of them showed that tin slows down the formation of radiation-generated centers connected with the $E_s = 0.2$ eV level. An assumption was made that the vacancies in tin-doped n-type germanium interact with both the tin and the antimony atoms by retarding the n-p conversion and stabilizing the life time of the nonessential charge carriers in the dose range studied. Figures 4; references 76; 5 Russian, 2 Western.

UDC 621.382

Patterns of Structural Defects Distribution in Semiconductors Beyond the Ion Retardation Zone Sphere During Ion Implantation

917M0018B Moscow *FIZIKA I KHIMIYA OBRABOTKI MATERIALOV* in Russian No 5, Sep-Oct 90 (manuscript received 19 Jul 89) pp 9-13

[Article by N.T. Kvasov, K.Yu. Yarashyunas, S.F. Spizhuk, and S.Yu. Shilina, Minsk]

[Abstract] Changes in the crystal structure that occur during ion implantation may occur in the immediate zone of ion retardation and far beyond this zone. Two models exist for the defect formation process beyond the ion retardation zone: the diffusion and shock models. The distribution of defects in silicon and indium antimonide beyond the ion retardation zone was studied after an ionic boron implantation. A determination of the structural damage profile was carried out by using

light diffraction on a light-induced lattice and light diffraction on ultrasound in the crystal. Both mechanisms of defect formation were observed, namely, the shock and the diffusion mechanisms. The shock mechanism dominated at greater distances; it was related to the interaction of elastic waves generated in the crystal during the implantation with the initial structure defects. The extent of the generated structural damage was found to be proportional to the inherent crystal imperfections. Figures 2; references 26; 25 Russian, 1 Western (by Russian authors).

UDC 535.21:621.375.826

Change in Optical Reflection From a Semiconductor Surface During Pulsed Laser Irradiation

917M0018C Moscow *FIZIKA I KHIMIYA OBRABOTKI MATERIALOV* in Russian No 5, Sep-Oct 90 (manuscript received 5 Apr 89) pp 14-17

[Article by S.V. Zhuk, G.G. Gromov, and V.B. Ufimtsev, Moscow]

[Abstract] A popular method for investigation of the dynamics of processes occurring in semiconductors as a result of laser irradiation is based on a study of the reflection coefficient expressed as a function of time, $R(t)$. Considerable temperature and concentration gradients of nonequilibrium charge carriers in the vicinity of the irradiated surface lead to a heterogeneous distribution of optical characteristics of the refraction and absorption indices (n and k). In the present work it was shown that consideration of this heterogeneity along with applying the Drude formula for the free carriers may lead to qualitatively different results of the $R(t)$ modelling. The calculated data agreed with the experimental values of the determination of reflection coefficients. The advantage of this approach in determining the optical characteristics of semiconductors is that it makes it possible to consider several effects that could occur during strong laser irradiation: a plasma effect, the formation of thin fusion layers, and accompanying interference effects. Figures 2; references 10; 7 Russian (2 by Western authors), 3 Western.

UDC 535.211

Modeling of Pulsed Periodic Laser Surface Alloying of Metal in a Gaseous Atmosphere

917M0018D Moscow *FIZIKA I KHIMIYA OBRABOTKI MATERIALOV* in Russian No 5, Sep-Oct 90 (manuscript received 1 Feb 89) pp 23-26

[Article by A.A. Uglov, A.G. Gnedovets, and O.M. Portnov, Moscow]

[Abstract] Laser surface alloying is a promising technology for treating various materials because it permits the formation of local zones with improved performance

characteristics: microhardness, wear resistance, etc. In the present paper results were reported of numerical modeling of pulsed-periodic laser alloying of a metal in an atmosphere of molecular gas. The iron-nitrogen system was selected as an example. The calculations were based on a kinetic model of the reaction of gas with the molten material. This type of laser irradiation produced nitrified diffusion layers in the iron several tens of microns thick. It was shown that the concentration profiles of the dopant exhibit maxima localized near the metal surface. Figures 2; references 6: 5 Russian, 1 Western.

UDC 541.15

The Formation of Stable Productions During the Radiolysis of Benzene in the Presence of α -Phenyl-N-tert-Butylnitron

917M0027A Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA in Russian Vol 31 No 5, Sep-Oct 90 (manuscript received 27 Feb 89) pp 488-491

[Article by V.V. Makhlyarchuk, V.Ye. Zubarev, and S.V. Zatonskiy, Radiation Chemistry Laboratory, Moscow University]

[Abstract] The method of capturing radicals by spin traps and recording the ESR spectra of the resultant adducts, which carry information regarding the nature of the captured radical, is widely used to study radical reactions in different systems and especially during liquid-phase radiolysis of aromatic hydrocarbons. The authors of the study reported herein are the first to

determine the effect of a spin trap on the formation of the main radiolysis products of α -phenyl-N-tert-butylnitron [PBN]. They irradiated deaerated solutions with a ^{60}Co γ -source with a dose strength of 3.5 Gy/s and with the maximum absorbed radiation dose amounting to 25 kGy. The first series of specimens were kept at room temperature for 2 days after irradiation, and the specimens in the second series were held at room temperature for 22 days. The radiolysis products were subjected to gas-liquid chromatographic analysis (as per the method described elsewhere) with a column temperature of 170° and a vapor source temperature of 200°. It was discovered that the presence of 0.05 M PBN in benzene results in a reduction in the total radiochemical yield of dimers (diphenyl and phenylcyclohexadiene) by about 0.06 molEq/100 eV. This value is in good agreement for the previously published value for pure benzene. The authors' research on the formation of radiolysis products of benzene containing a PBN spin trap made it possible to conclude that only part of the diphenyl and phenylcyclohexadiene (about 0.03 molEq/100 eV) forms as a result of radical reactions, whereas about 0.11 molEq/100 eV of the dimer products form via the nonradical route. Their research further demonstrated that the secondary and side reactions occurring during the radiolysis of benzene that involve PBN are significant. The research conducted demonstrated that research on the formation of the stable radiolysis products of organic systems containing spin traps in combination with an examination of the ESR spectra of their radical adducts may prove very fruitful in establishing the mechanisms of the radiochemical transformations of organic compounds. Tables 2; references 10: 6 Russian, 10 Western.

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